

REPORT No. 40.

THE FERROSILICON PROCESS FOR THE GENERATION OF HYDROGEN.

PART I.—GENERATION OF HYDROGEN FROM FERROSILICON AND SODIUM HYDROXIDE. By E. R. Weaver, W. M. Berry, and B. L. Bohannon.

PART II.—THE EFFECT OF THE PRESENCE OF SODIUM CARBONATE ON THE GENERATION OF HYDROGEN FROM FERROSILICON AND SODIUM HYDROXIDE. By E. R. Weaver and B. D. Gordon.

PART III.—THE USE OF LIME IN THE GENERATION OF HYDROXIDE BY THE USE OF FERROSILICON. By B. D. Gordon.

PART I.

GENERATION OF HYDROGEN FROM FERROSILICON AND SODIUM HYDROXIDE.

By E. R. WEAVER, W. M. BERRY, and V. L. BOHANNON.

A. PURPOSE AND SCOPE OF THIS PAPER.

This report was prepared at the Bureau of Standards for the National Advisory Committee for Aeronautics.

The generation of hydrogen by the reaction between ferrosilicon, sodium hydroxide, and water has been extensively employed in recent years for filling military and naval balloons. The method is understood to have been used much more generally abroad than by the American forces.

The ferrosilicon method is especially adapted for use in the field because of the relatively small size and low cost of the generator required to produce hydrogen at a rapid rate, the small operating force required, and the fact that no power is used except the small amount required to operate the stirring and pumping machinery. These advantages make it possible to quickly generate sufficient hydrogen to fill a balloon with a generator which can be transported on a motor truck.

The fact that none of the materials used are by themselves combustible, that they do not give off hydrogen until mixed, and that they are easily and safely transported and handled, makes the method especially safe and valuable for use aboard ship. The low cost of the generating plant also makes the method of value for shore stations where the demand for hydrogen is very irregular and the cost of an electrolytic or other plant capable of meeting the maximum demand would be excessive.

In order to determine the best conditions for the operation of hydrogen generators using this method, a large number of laboratory experiments have been made with various grades of ferrosilicon under many conditions. This report includes the results of these experiments, and some additional thermochemical data from which the effect of any variation in generator operation may be estimated by calculation, illustrative problems showing the application of the data, a discussion of all the conditions of operation from a theoretical standpoint, and a set of tentative directions for the purchase of ferrosilicon and the operation of the generator, all conclusions being based upon calculation and laboratory experiment.

B. GENERAL DESCRIPTION OF EXPERIMENTS.

1. *Materials used.*—Five 10-pound samples and one barrel of ferrosilicon obtained from the Electro Metallurgical Co., two 10-pound samples of lump ferrosilicon of high silicon content obtained from the Carborundum Co., and two very finely ground samples of unknown origin sent in for test were used in the experiments. The five samples from the Electro Metallurgical Co. had evidently been crushed to pass a screen of about 16 meshes per inch. When screened each sample gave approximately the following proportions of the various sizes:

- 10 per cent failed to pass a 20-mesh screen.
- 20 per cent passed a 20-mesh, but failed to pass a 30-mesh.
- 10 per cent passed a 30-mesh, but failed to pass a 40-mesh.
- 10 per cent passed a 40-mesh, but failed to pass a 60-mesh.
- 15 per cent passed a 60-mesh, but failed to pass an 80-mesh.
- 15 per cent passed an 80-mesh, but failed to pass a 100-mesh.
- 20 per cent passed a 100-mesh.

The silicon present in one or more portions of each material was determined by the usual gravimetric method for silicon in ferrosilicon with the following results, each of which is the average of two or more fairly concordant determinations:

Sample No.	Origin.	Fineness.		Silicon.	
		Mesh.		Per cent.	
1	Electro Metallurgical Co.	20-30		84.0	
2	do	20-30		80.9	
3	do	20-30		60.1	
4	do	20-30		71.5	
5	do	20-30		85.5	
6	do	20-30		88.7	
7	do	100		79.1	
8	Carborundum Co.	20-30		95.1	
9	do	20-30		99.0	
10	Unknown	100		89.7	
	do	100		91.4	

The fact that the fine material of sample 6 shows a lower silicon content than the 20-30-mesh material may be explained by the assumption that it consists in part of slag which, being more brittle than the alloy, would be more easily powdered. This assumption is borne out by the low yield of hydrogen from this and every other fine sample from the sifted materials.

2. *Methods of experiment.*—The experiments from which the more important conclusions were drawn were of two kinds, those made to determine the total yield of hydrogen and those made to determine rate of evolution of hydrogen.

The apparatus shown in figure 1 was used to determine total hydrogen yield. A weighed sample, about 2 grams, of the material to be tested was introduced into A and covered with water. The flask was then evacuated and the water boiled vigorously to expel air. A considerable excess of sodium hydroxide solution was then slowly introduced. After violent reaction ceased the solution was boiled for one hour or longer. The gas evolved was then measured in bottle C by determining the amount of water displaced. The total yield of hydrogen was found to be independent of the concentration and amount of sodium hydroxide solution used, provided there was present at least the amount indicated as required by the equation



It was also found that for the grades of material containing more than 75 per cent silicon the amount of hydrogen evolved after the first hour was negligible.

The more important experiments upon the rate of reaction were made in the following manner: The body of a spherical 3-liter flask was immersed in a water bath through which steam could be forced to control the temperature. The flask was connected through a water-cooled condenser and a shallow water seal to a gas meter. The solution to be tested was introduced and brought to the desired temperature, usually 100° C. A weighed amount of ferrosilicon was then added through a large-stemmed funnel and the opening through which the funnel was inserted quickly closed. As soon as the meter began to move, a stop watch was started and the meter reading recorded at intervals, usually of one minute. After the run the yield was plotted against time. Figure 2 is a characteristic curve showing the results obtained in one such test. In most cases comparative rates only were wanted. The average rate between the first and second or first and third minute was usually taken for comparison. This particular interval was chosen, first, to avoid so far as possible errors of judgment as to the time of starting, and, second, to obtain results very near the starting time, before large changes could occur in the temperature or in the amount of ferrosilicon unacted upon. Variations from these general methods of experiment will be noted in connection with a discussion of the data obtained.

C. EXPERIMENTAL AND COMPILED DATA.

1. *Relation of composition of ferrosilicon to total hydrogen yield.*—Figure 3 shows the total yield of hydrogen from each of the 11 samples of ferrosilicon for which the analyses are given above. The determinations were made as described under "Methods of experiment," except

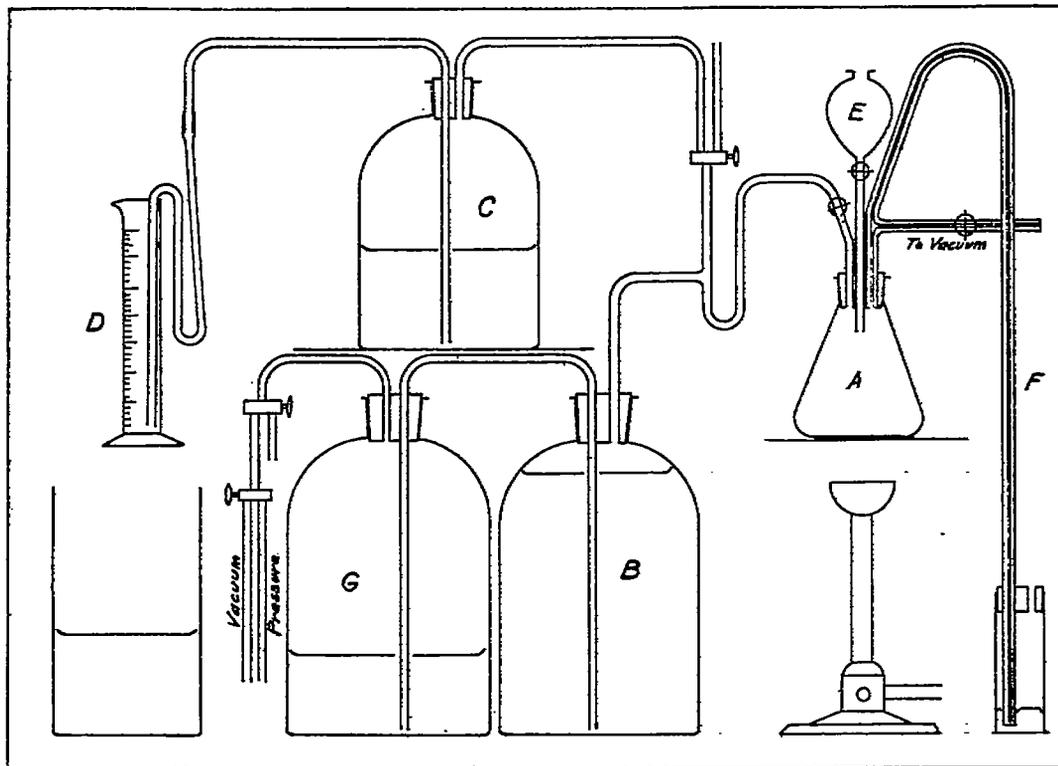
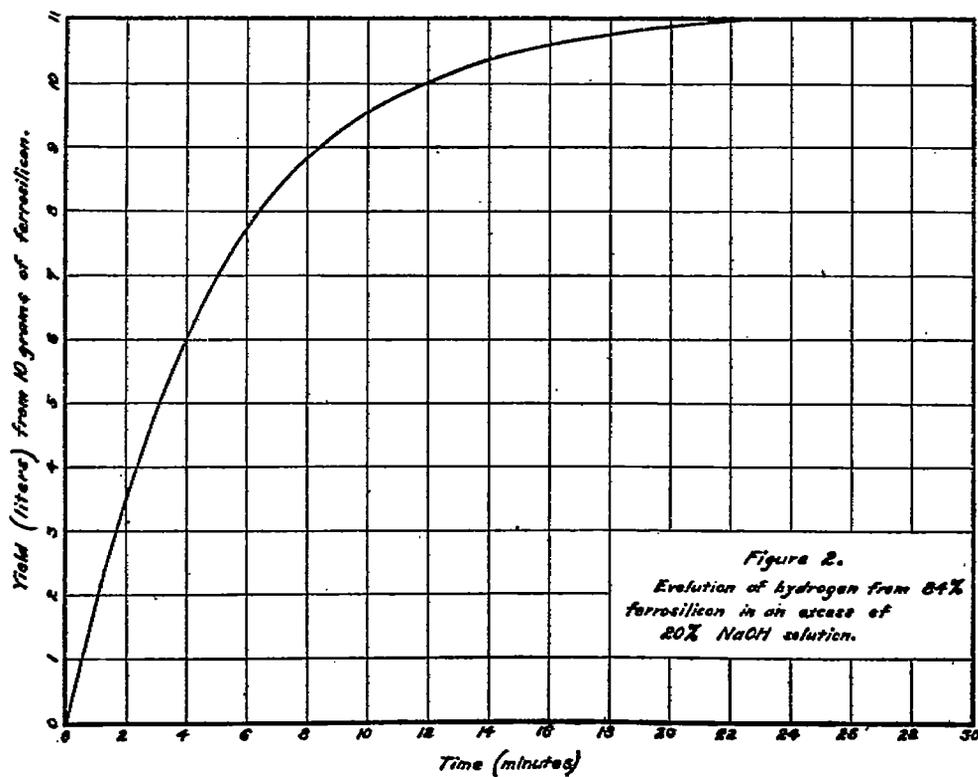
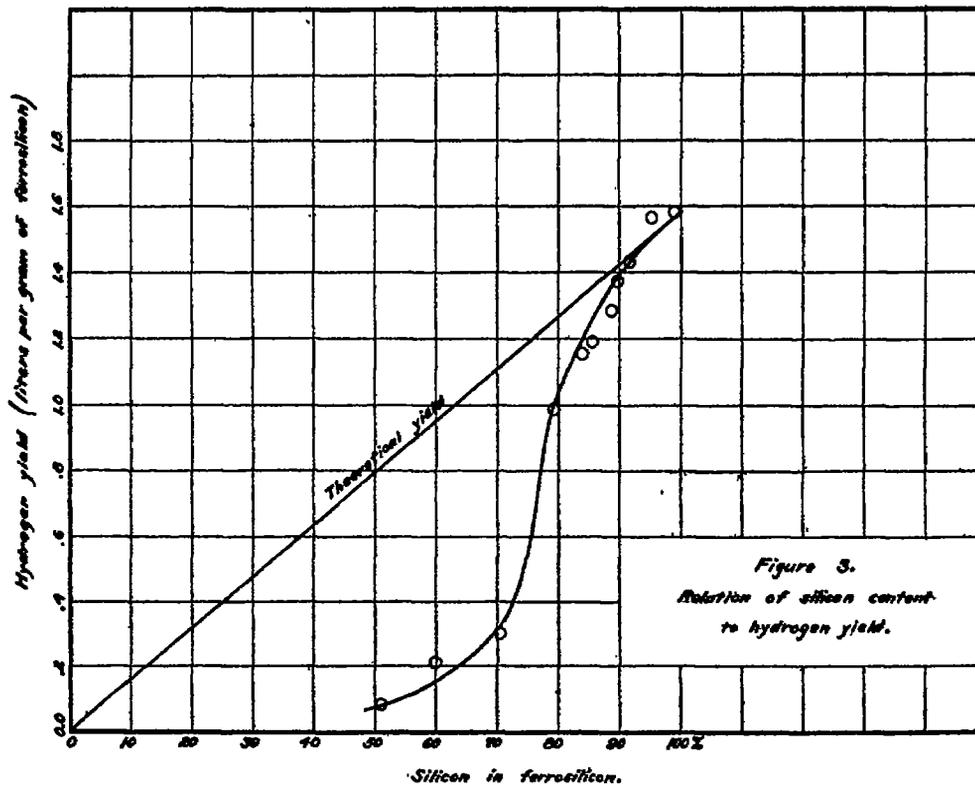


FIG. 1.—Apparatus for the determination of total hydrogen yield.



that the materials below 75 per cent, which did not react vigorously at any time, were boiled for the uniform period of an hour and a half instead of for "one hour after vigorous reaction ceased." It will be noted that with materials of less than about 75 per cent silicon content the gas yield decreases much more rapidly than the percentage of silicon. The steep portion of the curve may in reality occur at a higher percentage than this, since the 79 per cent material was probably made up of a mixture of 85-90 per cent ferrosilicon with more or less inert material. The use of material containing not less than 75 per cent of silicon seems necessary; and, in fact, a higher percentage may be of material advantage.

The reaction is very rapid at first and gradually slows down, but continues for many hours. The end of the reaction is therefore indefinite, but the amount of hydrogen evolved after the first 15 minutes is only a small fraction of the total. In addition to the silicon, some of the



iron and probably all of the aluminum present in the alloy go into solution with the evolution of hydrogen. Since some of the hydrogen is produced from materials other than silicon and some of the silicon present may be in the form of silica (SiO_2) or metallic silicates, which do not react with water to produce hydrogen, it is not surprising to find that the silicon content of a sample of ferrosilicon is not an exact measure of the hydrogen which will be given off under operating conditions.

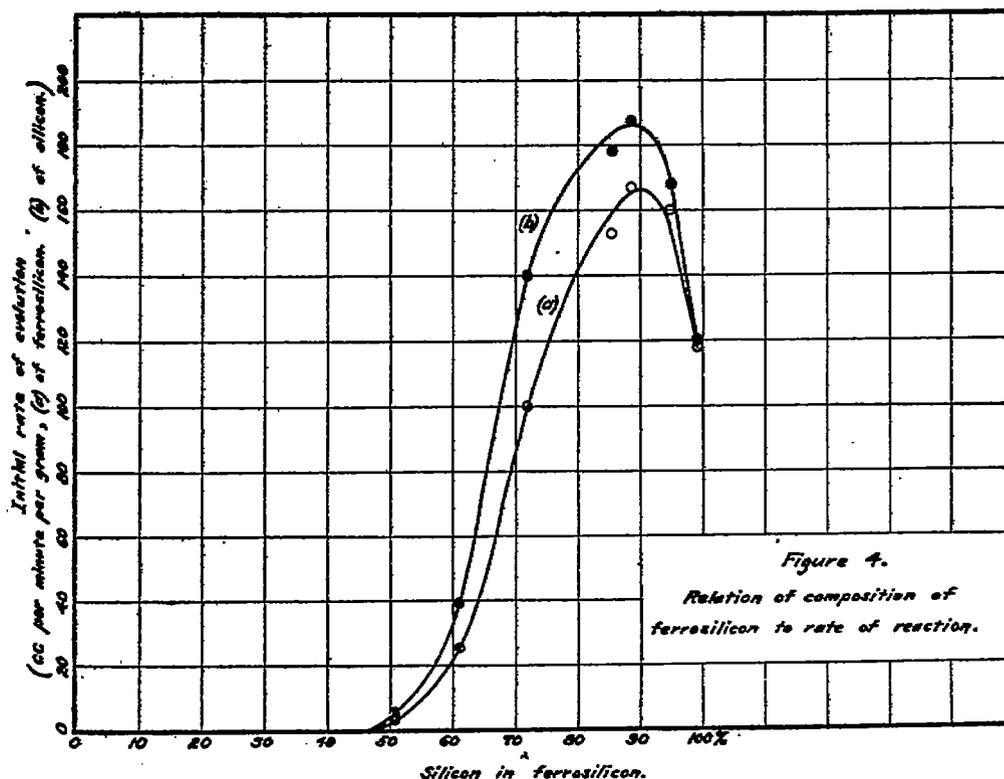
By screening out a uniform sample of coarse material, grinding part of the sample completely to a fine powder, and determining yield of hydrogen in both portions, it was found that the total yield is independent of the fineness of the sample.

2. *Relation of composition of ferrosilicon to rate of reaction.*—Figure 4 shows the relation of the percentage of silicon in the ferrosilicon to the initial rate at which hydrogen is evolved. The experiments were made in the manner described under "Method of experiment"; the same weight of 20-30-mesh materials of different composition was introduced into an excess of 20 per cent sodium hydroxide solution maintained at 100°C . and the rates were compared over the interval between the first and third minutes after the reaction began.

The important facts established by these experiments are (1) that the rate of reaction falls off very rapidly when the percentage of silicon is decreased below 70 or 75 per cent, and (2) that the rate of reaction is lower for nearly pure silicon than for material containing about 90 per cent of silicon.

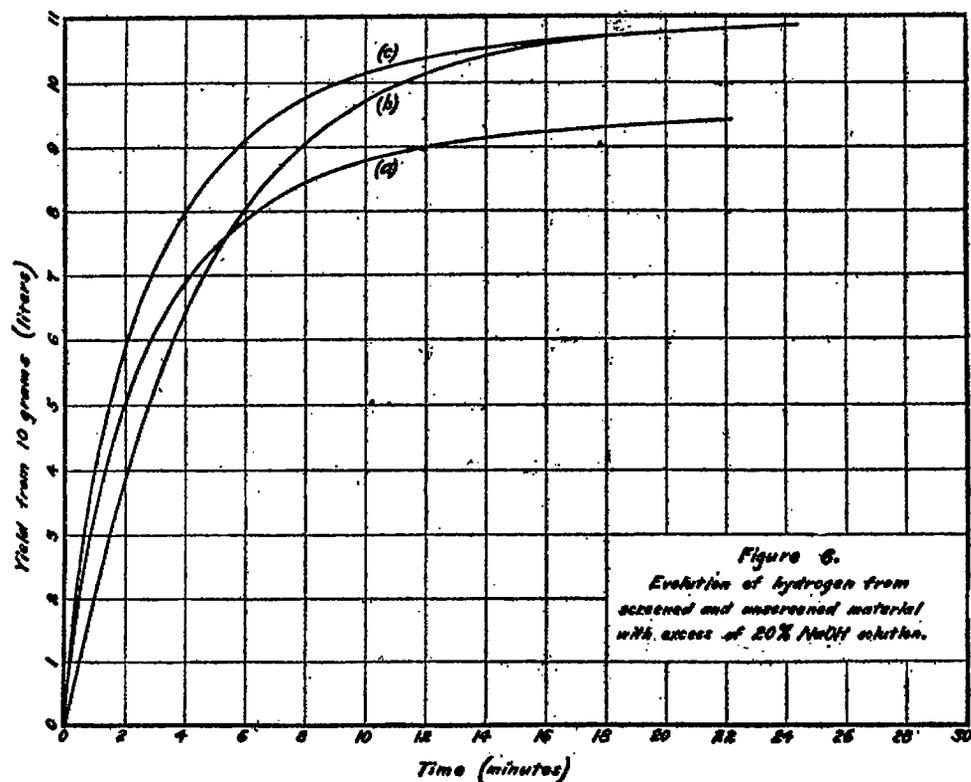
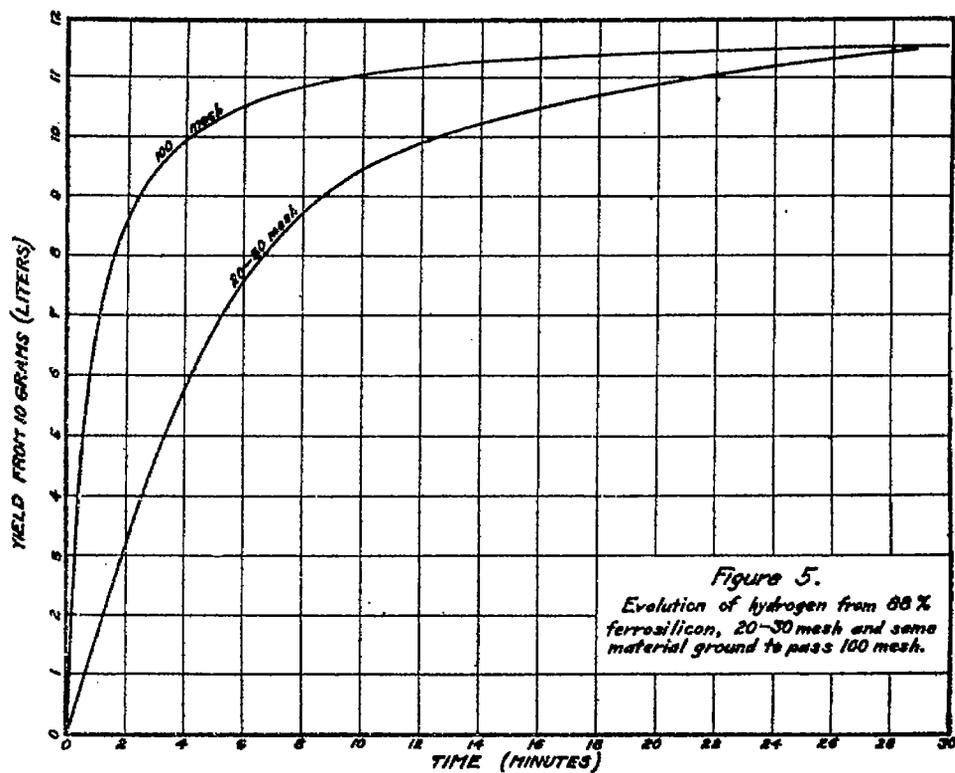
The slow rate of reaction of nearly pure silicon is probably due to the presence of the graphitic form which is much less readily attacked by chemical reagents than the amorphous form. The amorphous form of silicon is probably the chief constituent of the lower grade materials.

3. *Effect of fineness of ferrosilicon upon rate of reaction.*—Experiments upon the relative rate of reaction of ferrosilicon of different degrees of finenesses and of the same composition were carried out in the same manner as the other rate experiments, using an excess of 20 per cent solution at a temperature of 100° C. Figure 5 shows two typical curves representing the



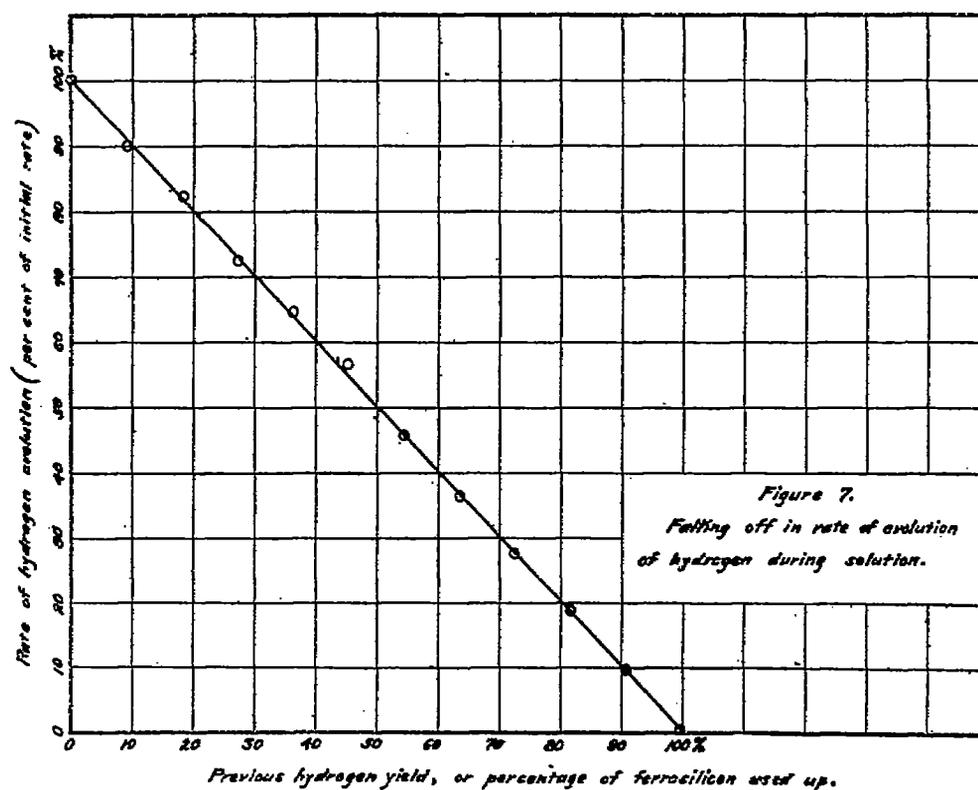
reaction of 20–30-mesh ferrosilicon containing 88.3 per cent of silicon and the same material after grinding to pass a 100-mesh sieve. It should be observed that the total yield is the same from the two samples, but the rates are different.

A comparative test of material of a uniform size and material containing large and small particles as it comes from the crusher was also desired. Such a comparison could not be made directly because of the very great difference in composition, and therefore in hydrogen yield between the coarse and the fine powder in each of the samples; an indirect comparison is shown in figure 6, however. In it (a) is an experimental curve showing the course of the reaction of the ferrosilicon taken directly from the barrel of ferrosilicon which had an average silicon content of about 70 per cent. An effort was made to have this sample represent the average fineness of the material in the barrel. Curve (b) is an experimental curve showing the reaction of that portion of the ferrosilicon from the barrel which passed a 20-mesh sieve, but not a 30-mesh sieve (sample No. 1, p. 4). It had been shown by experiment (cf. fig. 5) that material of the same composition gives the same total yield whatever the fineness. The total yield obtained in these experiments from the material of mixed sizes is 0.95 liter per gram; that from



20-30-mesh material 1.1 liters per gram. Assuming the rate of reaction proportional to the composition (a relation indicated by fig. 4 as being approximately true for ferrosilicon of this composition and one which should be exactly true if the finer material is low in silicon because of the presence of inert particles) curve *C* was plotted with ordinates obtained by multiplying the ordinates of curve (*A*) by 1.1/0.95. Curve *C* therefore represents approximately the rate of reaction of 84 per cent material crushed to the average of fineness of the material in the barrel.

4. *Decrease in rate of reaction with exhaustion of ferrosilicon.*—Figure 7 represents the relation between the rate of evolution of gas and the amount of ferrosilicon remaining undissolved throughout the reaction. Since it is possible to determine the stage of the reaction only by observing the volume of gas produced, the data are given in terms of rate of reaction and previous hydrogen yield. The small circles, representing the observed data for a single typical case, fall on the straight line within the limit of error of observation, and show that the rate of evolution is at all times directly proportional to the amount of ferrosilicon

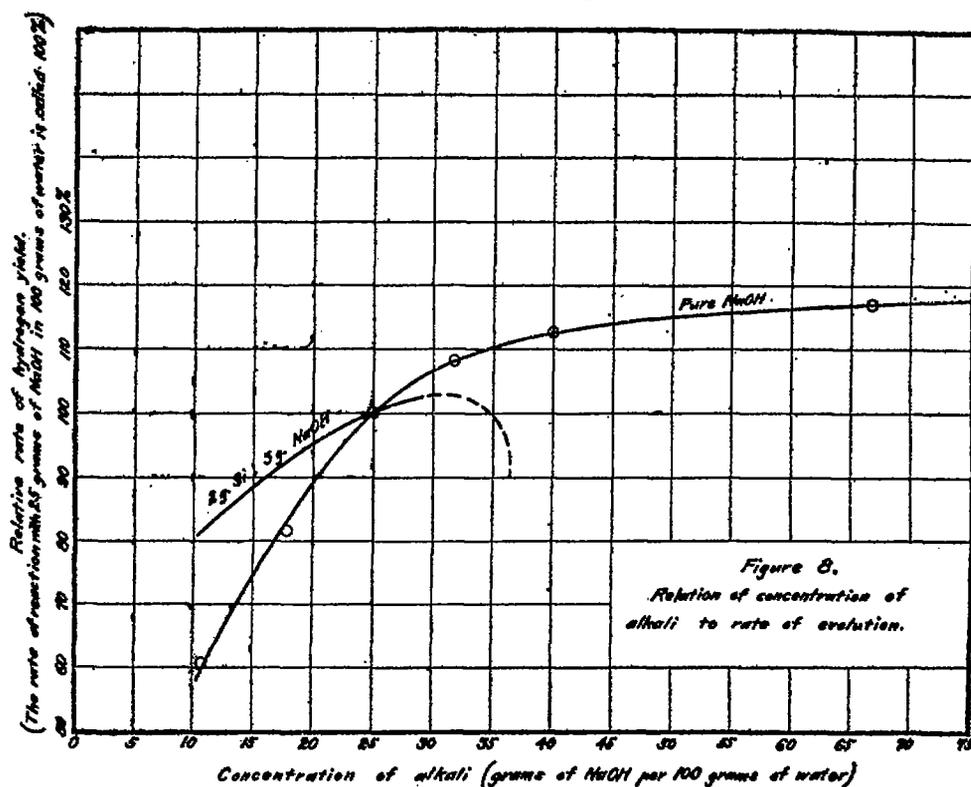


remaining unattacked. Corresponding data were plotted for material of several degrees of fineness and for a mixture of all finenesses occurring in the crushed material, and the same relation was found to hold.

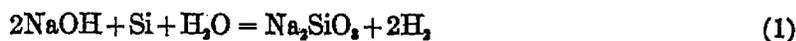
This relation is important, since it enables us, after once determining the initial rate of reaction and the total yield for a given sample of ferrosilicon, to calculate with considerable accuracy the rate of reaction after any given amount of hydrogen has been evolved. Or, in other words, knowing this relation it is possible to predict the speed of reaction at any stage of the evolution of gas.

5. *Relation of concentration of sodium hydroxide solution to rate of reaction.*—By a series of tests similar to the rate experiments previously described, but in each of which the same amount of ferrosilicon of the same composition and fineness was added to a large excess of sodium hydroxide dissolved in a different amount of water, the approximate effect of concentration of alkali upon the rate of evolution was determined. The curve labeled "pure NaOH" in figure 8 represents the relative rates of evolution at the beginning of the runs

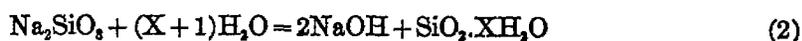
In order to investigate the rate of reaction with the solutions remaining after some ferrosilicon has already reacted, a series of experiments were made with solutions in which various amounts of sodium hydroxide and ferrosilicon were allowed to completely react in a weighed flask in a steam bath. The solutions were then brought to any desired concentration by weighing the flasks and adding known weights of water. The flasks were then connected to the meter through the condenser and heated with steam until no more bubbles of gas were expelled from the flask. A weighed amount of fresh ferrosilicon was then introduced and the initial rate of evolution of hydrogen determined as in previous experiments. In every case concentrated solutions showed more rapid rates of evolution than more dilute ones up to the concentration at which the solutions appeared noticeably gummy. Above that concentration the rate of evolution rapidly fell off. The second curve in figure 8, labeled "2gSi: 3gNaOH," shows the approximate effect of dilution upon solutions containing two parts by weight of dissolved silicon to three parts of sodium hydroxide originally present.



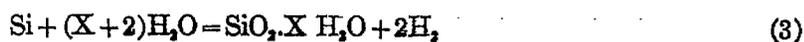
6. *Relation of amount of alkali to rate of reaction.*—The production of hydrogen from ferrosilicon may be represented by the equation

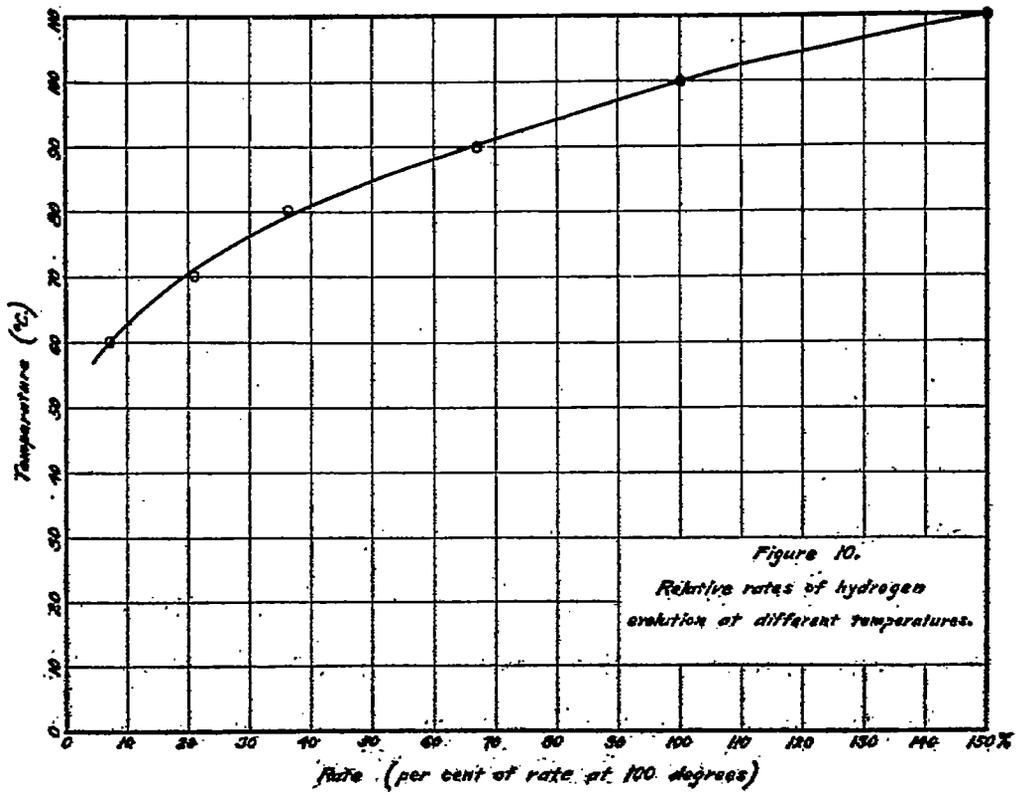
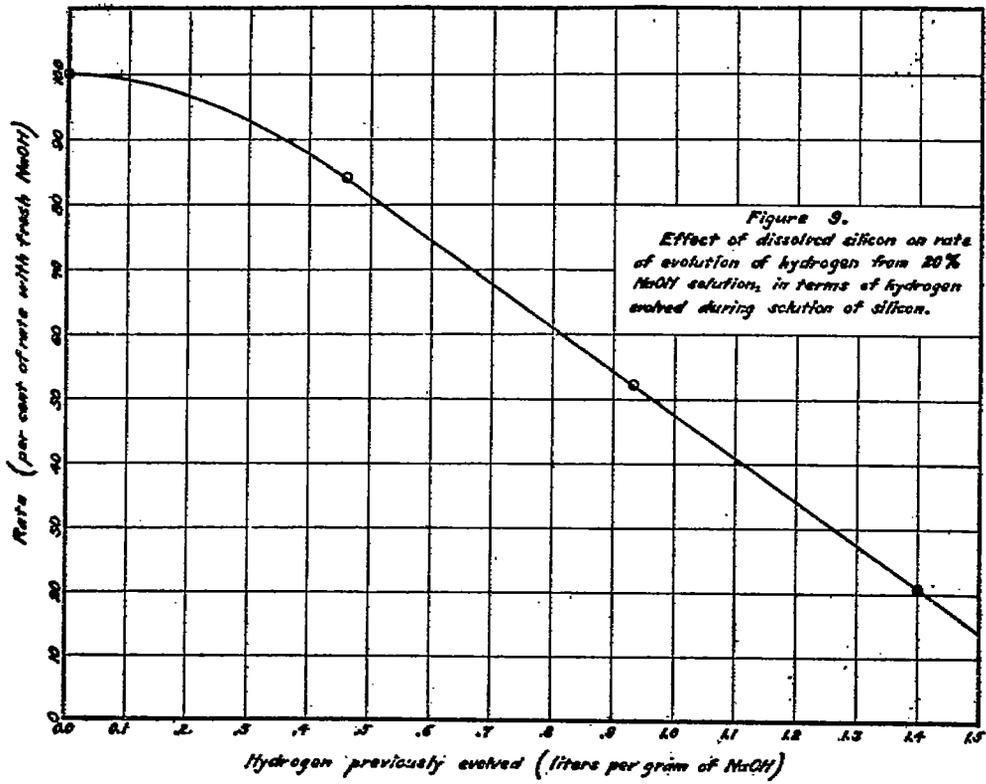


According to this equation the weight of alkali required to react with ferrosilicon would be approximately 2.8 times the weight of silicon contained. Equation (1) probably represents the reaction taking place at the beginning of a run. However, sodium silicate in solution hydrolyzes, giving sodium hydroxide and hydrated silicic acid as indicated by the equation



If we combine equations (1) and (2) we get the equation





Although the compounds specified may not be the only ones formed they are typical of the course of the reaction. The ultimate reaction may therefore be regarded as one between silicon and water in which the alkali acts as a catalyst. This viewpoint is important, since it explains the observed production of hydrogen in excess of the amount which could be obtained from a given weight of sodium hydroxide according to equation (1) and shows that the relative amounts of alkali and ferrosilicon to be used in practice should be determined by the rate of evolution of the gas and the relative cost of ferrosilicon and alkali rather than by computing the equivalent proportions corresponding to a definite chemical equation.

It is evident that the rate of reaction at the beginning of a run should depend only upon the concentration of the sodium hydroxide solution, and not at all upon the amount present, provided of course there is enough to wet all the solid surface. The question to be answered by experiment is, how does this initial rate fall off as the alkali becomes exhausted. The experiments described in the preceding section, in which definite weights of sodium hydroxide and ferrosilicon were allowed to completely react and the rate of evolution of gas from a fresh sample of ferrosilicon was then determined, gave results showing also the effect upon the rate of reaction of partially exhausting the sodium hydroxide. The results obtained when using a 20 per cent sodium hydroxide solution are shown in figure 9. The relative decrease in the rate of evolution with the exhaustion of the sodium hydroxide was of the same order of magnitude for other concentrations up to the point at which the solutions became very viscous.

7. *Effect of temperature upon rate of reaction.*—The results of experiments upon the effect of temperature upon the relative rates of reaction are shown in figure 10. These experiments were made by dropping a single grade and fineness of ferrosilicon into a very large excess of 20 per cent sodium hydroxide solution and observing the time required to produce a given volume of gas, the temperature being kept constant to within one or two tenths of a degree during the interval. This was considered a better method than determining the yield over a definite interval of time on account of the great difference in rates in these experiments. If the latter method had been used, the interval for comparison would have had to be either so long that the rate for the higher temperatures would have fallen off through the exhaustion of the material or so short that the volumes evolved at the lower temperatures could not have been measured with sufficient accuracy.

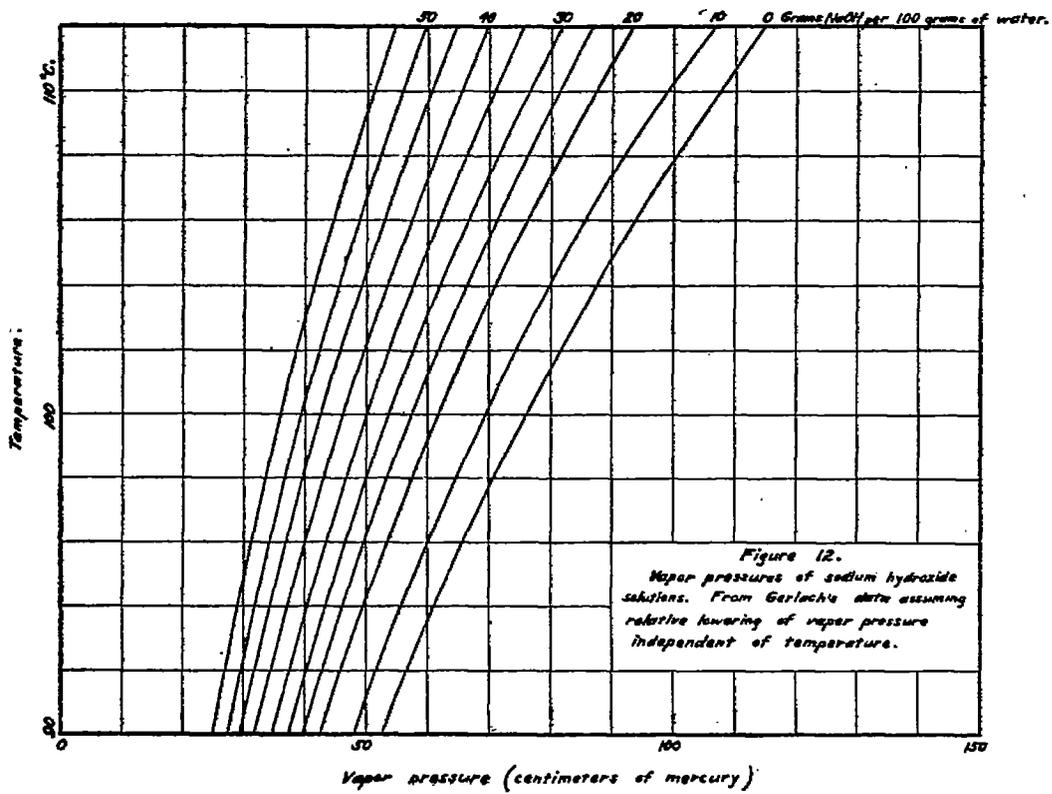
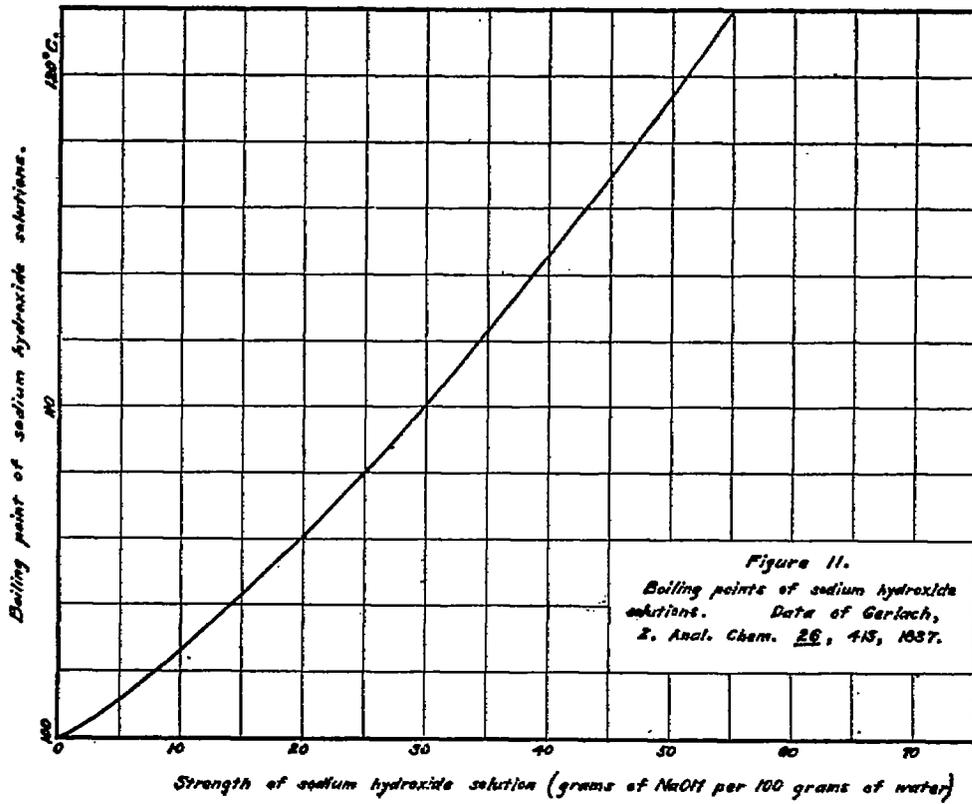
8. *Thermal properties of sodium hydroxide solutions.*—Graphs 11, 12, 13, and 14 give, in convenient form, data regarding the heat of solution, specific heat, boiling point, and vapor pressure of sodium hydroxide solutions of various strengths. All the data are taken from the "Landolt-Börnstein Physikalisch Chemische Tabellen" with the exception of the vapor pressure curves of figure 12. These are computed from the data used for figure 11 and the vapor pressure of water on the assumption that the ratio of the vapor pressure of the solution to that of pure water is independent of the temperature.

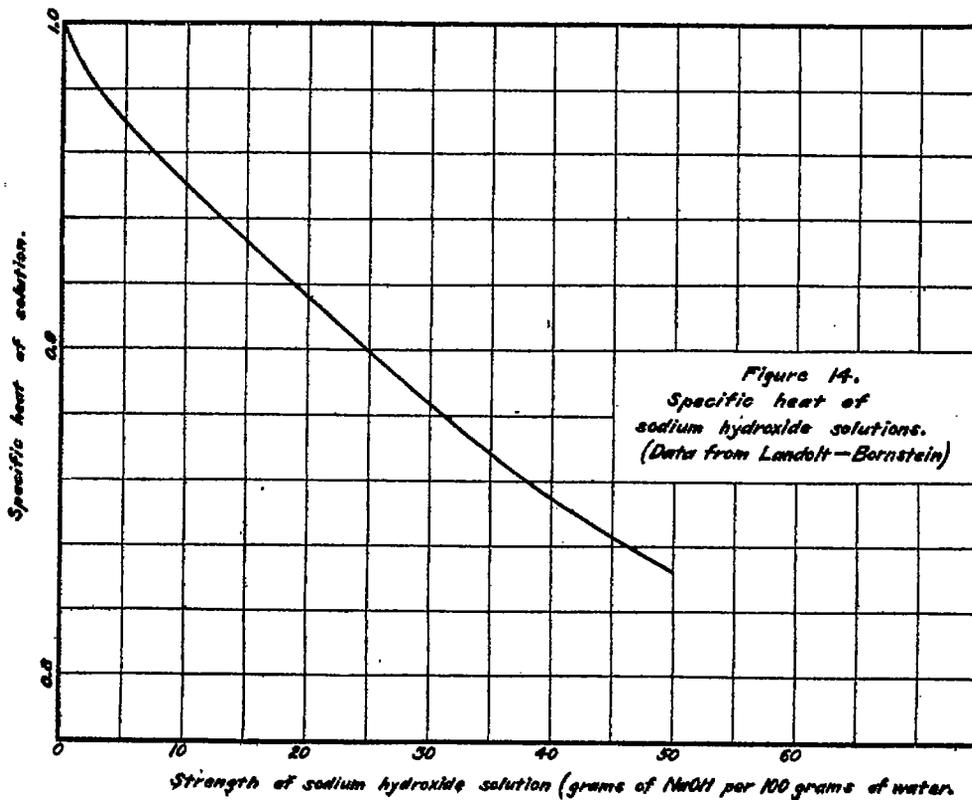
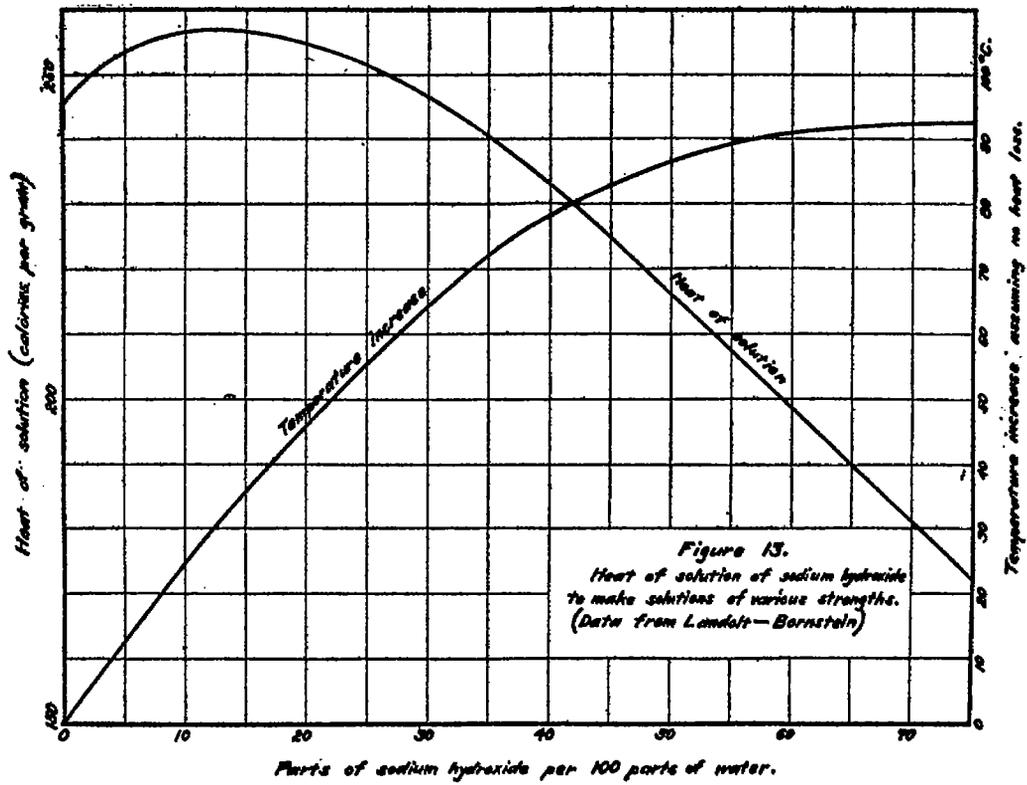
D. THE FIELD GENERATOR.

1. *Description of generator.*—The ferrosilicon method is used almost exclusively for the generation of hydrogen for filling balloons in the field, on board ship, or at small naval shore stations.

The plant required for the production of hydrogen consists of three principal parts—(1) the solution tank in which the sodium hydroxide is dissolved, (2) the generator proper in which the reaction takes place, and (3) the washer or condenser in which the evolved gas is washed with water and cooled before being stored or being put into the balloon. The parts are so arranged that liquid can be run into the generator from the solution tank by gravity. The generator is usually provided with an adjustable feed mechanism which places the ferrosilicon feed under the immediate control of the operator. A cold-water spray for diluting the contents of the generator and regulating its temperature is also provided.

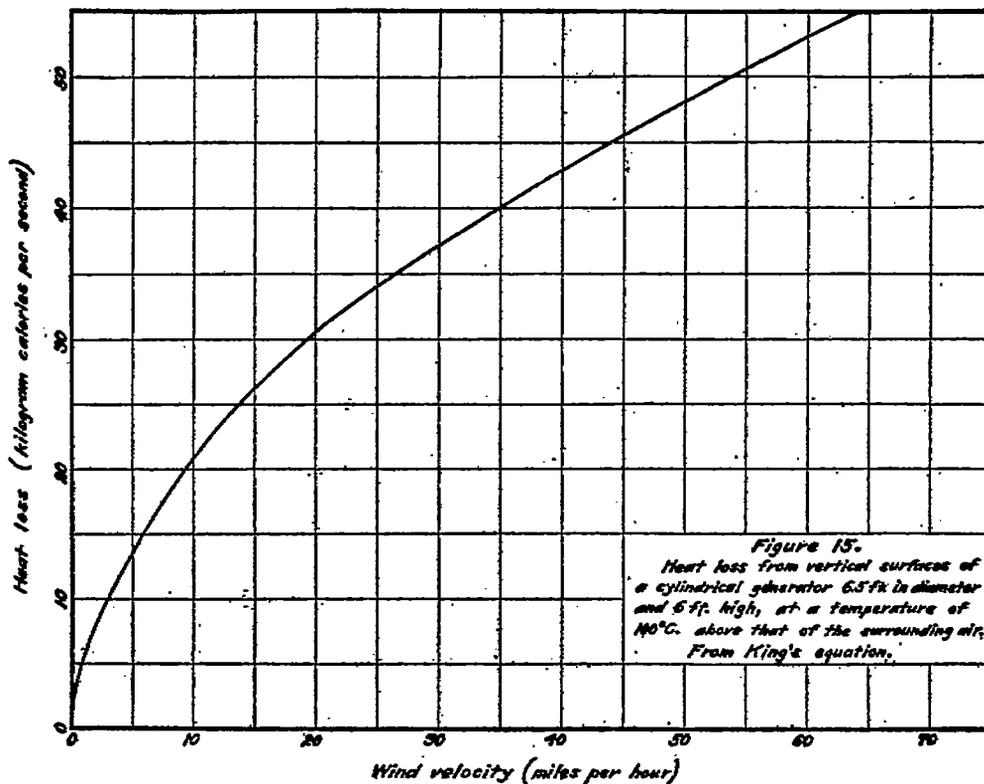
The operation of the generator is as follows: A predetermined charge of sodium hydroxide and water are stirred together in the solution tank until solution is complete. A part or all of the solution is then run into the generator and ferrosilicon added at such a rate as will best





control the evolution of the gas. The heat of solution of sodium hydroxide is sufficient to start the reaction with ferrosilicon. The heat of this reaction increases the temperature rapidly, a large amount of water is evaporated, and it soon becomes necessary to both cool and dilute the contents of the generator. This is done by means of the water spray mentioned in the preceding paragraph. Care must be taken throughout the reaction that the contents of the generator do not foam over and that the hydrogen does not pass through the washer at too rapid a rate and so carry sodium hydroxide spray and water into the balloon.

At the best the cost of materials makes the ferrosilicon method expensive in comparison with several other methods of generating hydrogen. The method has, however, several great advantages; a very rapid rate of hydrogen production can be secured from a comparatively small and inexpensive plant with very little labor and only sufficient power to operate the water pumps and stirring machinery. The advantages and limitations of the method, therefore, make it suitable only for portable plants and small stationary units where the cost of a larger



but more efficient plant is not justified. The following sections dealing with the practical application of theory and laboratory experiment are written with special reference to portable generators of about the maximum size which can be conveniently transported on a motor truck. For the purpose of the following discussion a hypothetical case is assumed in which a generator having a diameter of 6 feet 6 inches and a height of 6 feet is chosen. It is also assumed that the generator sides and bottom are of $\frac{1}{4}$ -inch sheet iron.

2. *Heat loss from surface of generator.*—The losses of heat from the surface of the generator are of considerable, but not primary, importance in determining the thermal conditions existing during the reaction. One of the most commonly accepted equations for loss of heat by convection from cylindrical surfaces is that of L. V. King.¹ This equation, for the case of the small temperature differences existing between the generator and the surrounding air, reduces to the following equation, representing the loss of heat from a cylinder exposed to air currents perpendicular to its axis.

$$w = 1.4 \times 10^{-8} \sqrt{r} (t_1 - t_2) \sqrt{v}$$

¹ Phil. Trans. Roy. Soc. (British), 214, p. 373-439, 1914.

Here w is the power loss in watts per centimeter of length of the cylinder, r is the radius of the cylinder in centimeters, t_1 and t_2 are the temperatures of the cylinder and of the surrounding air, respectively, and v is the air velocity in centimeters per second.

This equation was derived from theoretical considerations, using constants determined by experiment upon electrically heated wires, and is known not to apply exactly to cylinders of large size.

From this equation the heat loss per second from the vertical surface of the generator in a wind blowing 50 miles per hour, the temperature of the generator being 120° F. above that of the air, would be 32,000 calories per second. From experiments in the Massachusetts Institute of Technology, discussed by J. C. Hunsaker,¹ the heat loss from an airplane radiator, with the same wind velocity and temperature difference, is found to be 0.86 B. t. u. per square foot per second. At this rate the loss from the generator under the assumed conditions would be 26,700 calories per second. Considering the great difference in the conditions of experiment, the agreement is satisfactory for our purpose, and King's equation may be used to give a probable maximum figure for the heat loss from the generator. The radiation from the same surface under the same conditions probably does not exceed 100 calories per second, the exact amount depending upon the condition of the surface, but being negligible in any case.

The curve in figure 15 was drawn from King's equation to represent the heat loss from 125 square feet of generator surface (approximately the area of the generator sides) at various wind velocities for a temperature difference of 100° C. The heat loss for zero wind velocity was taken from the figure in Kent's Mechanical Engineer's Handbook for the heat loss per square foot of surface from steam and hot-water radiators.

3. *Heat capacity of generator.*—The heat capacity of the generator was calculated from the weight of iron in the sides and bottom of the tank and the specific heat of iron. The weight of metal was computed to be about 550 kilograms and its heat capacity equal to that of about 66 kilograms of water.

E. APPLICATION OF EXPERIMENTAL RESULTS TO GENERATOR OPERATION.

The application of the data given in Part C of this report to the problems of generator operation can probably be best shown by one or more examples. In the following problems a complicated set of conditions is chosen for illustrative purposes only; it is not the intention to recommend that the operating conditions assumed here be followed in practice.

1. *Typical generator problem No. 1.*—Assume the following weather conditions to prevail:

Air temperature.....	20° C.
Water-supply temperature.....	18° C.
Barometer.....	740 mm. of mercury.
Wind velocity.....	10 miles per hour.

The charge is to consist of 800 pounds of ferrosilicon of the composition of the barreled material used in the experiments shown in figure 6 crushed to pass a 16-mesh sieve.

Generation is started with a 30 per cent sodium hydroxide solution made from 640 pounds of sodium hydroxide dissolved in 1,493 pounds of water. In order to heat the solution more quickly to the desired temperature of reaction, only half the solution and 75 pounds of ferrosilicon are introduced into the generator at the start. When the temperature reaches 90° C. the ferrosilicon feed is started at the uniform rate of 15 pounds per minute and continued until the charge has all been added. As soon as the ferrosilicon feed is started, the remainder of the solution is run into the generator at such a rate as to keep the temperature constant. When all the solution has been added, water is run in until the solution contains about 20 per cent of sodium hydroxide. The water spray is then stopped and no further effort made to control the generation until the charge is exhausted.

640 pounds NaOH=	$640 \times 0.454=290$ kg.
1,493 pounds water=	$1,493 \times 0.454=677$ kg.
Total weight of solution=	$290+677=967$ kg.

¹ Aerial Age Weekly, May 29, 1916.

The solution contains $290/677=42.8$ parts of sodium hydroxide per hundred of water. From figure 13 we find the heat of solution of sodium hydroxide in a solution of this strength to be 232 calories per gram, which is equal to the same number of kilogram-calories per kilogram. The total heat of solution available is therefore

$$290 \times 232 = 67300 \text{ kilogram-calories.}$$

Of this amount $2 \times 677 = 1,354$ kilogram-calories is required to raise the temperature of the water to the air temperature, 20° . The specific heat of the solution is found to be 0.85 (fig. 14). The total heat capacity of the solution is therefore equivalent to

$$0.85 \times 967 = 822 \text{ kg. of water.}$$

Assume that the heat capacity of the mixing tank is about three-fourths that of the generator or equivalent to about 50 kilograms of water. If there were no heat lost to the surroundings, the temperature would rise

$$\frac{67300 - 1354}{50 + 822} = 75^\circ \text{ approximately.}$$

Assume that the average temperature of the solution during mixing is half as much above the surroundings and that solution is complete in 20 minutes. The surface losses from the mixing tank will approximate those from the generator for the same temperature conditions. The surface loss for a temperature difference of 100° in a 10-mile wind is about 20 kilogram-calories per second (fig. 15). The total loss during the interval is about

$$0.375 \times 20 \times 20 \times 60 = 9000 \text{ kilogram-calories.}$$

When introduced into the generator the temperature of the solution is therefore

$$\frac{67300 - 10354}{872} = 65^\circ$$

above that of the surrounding air. The heat capacity of the generator was computed to be equal to that of about 66 kilograms of water and the heat capacity of the 75 pounds (equal to 34.1 kilograms) of ferrosilicon is equal to about 5 kilograms of water.

One-half of the solution has a heat capacity equal to that of 411 kilograms of water. When this amount is run into the generator, and the ferrosilicon added, the initial temperature is therefore about

$$\frac{411 \times 65}{411 + 71} = 55.8^\circ$$

above that of the air or 75.8° C.

The rate of hydrogen evolution from the ferrosilicon used, in 20 per cent sodium hydroxide solution at 100° C., was found to be 0.35 cubic meters per kilogram per minute when the gas is measured dry at 0° C. and 760 millimeters pressure (fig. 6). At 75.8° the rate of reaction is 29.5 per cent as fast as at 100° (fig. 10); for brevity the "temperature factor" is 0.295.

In 30 per cent solution the rate is about 113 per cent of the rate in 20 per cent solution (fig. 8); the "concentration factor" is 1.13. The rate of evolution from the 34.1 kilograms of ferrosilicon initially present is therefore $0.35 \times 34.1 \times 0.295 \times 1.13 = 3.98$ cubic meters per minute. One gram molecule of silicon when dissolved in sodium hydroxide solution produces 44.8 liters of hydrogen with the evolution of 49 kilogram-calories. The total heat of reaction during the first minute is therefore

$$\frac{3980 \times 49}{44.8} = 4360 \text{ kilogram-calories.}$$

The boiling point of 30 per cent sodium hydroxide solution is 115.3° C. (fig. 11). The vapor pressure of water at 115.3° C. is 1,280 millimeters; that of the solution is, of course, 760 millimeters. The vapor pressure of water at 75.8° C. is 299 millimeters. Then the vapor pressure of the solution at 75.8° C. is about

$$\frac{299 \times 760}{1280} = 178 \text{ millimeters.}$$

The barometric pressure is 740 millimeters. Consequently the gas leaving the generator is made up of water vapor and hydrogen in the proportion by volume

$$178 : 740 - 178.$$

There is therefore

$$\frac{178 \times 3.98}{(740 - 178) \times 22.4} \text{ kilogram molecules, or}$$

$$\frac{178 \times 3.98 \times 18}{(740 - 178) \times 22.4} = 1.0 \text{ kilogram of water in the escaping gas.}$$

The heat of vaporization of pure water is 536 kilogram-calories per kilogram. From figure 14 it is apparent that the heat of vaporization of water from a 30 per cent sodium hydroxide solution is less than 0.2 kilogram-calories greater than from pure water. The total heat of vaporization involved is therefore about 540 kilogram-calories.

The heat loss from the surface of the generator is about $(75.8 - 20) \times 0.21 \times 60 = 700$ kilogram-calories. The total heat lost by evaporation, convection, and radiation is therefore about 1,240 kilogram-calories compared with the 4,360 kilogram-calories produced by the reaction, leaving 3,120 kilogram-calories available to raise the temperature of the generator and its contents. The temperature increase is therefore

$$\frac{3120}{411 + 71} = 6.5^\circ \text{ approximately.}$$

At the beginning of the second minute the temperature is therefore

$$75.8 + 6.5 = 82.3^\circ.$$

The new temperature factor is found to be 0.43. The concentration of the solution has not changed materially; consequently the concentration factor remains the same. There is no longer 34.1 kilograms of ferrosilicon present, however. Figure 6 shows that the total hydrogen yield from ferrosilicon of this quality is about 0.95 liter per gram or 0.95 cubic meter per kilogram. The 34.1 kilograms have already produced 3.98 cubic meters out of a possible 34.1×0.95 . The rate of reaction is therefore only

$$100 - \frac{3.98}{34.1 \times 0.95} = 87.7 \text{ per cent}$$

as fast as the original rate (fig. 7). The number 0.877 represents the ratio of the surface now present to the original surface and is called the "surface factor."

The rate of reaction is also affected by the fact that some of the sodium hydroxide has been used to form sodium silicate. From the volume of hydrogen produced per kilogram of sodium hydroxide,

$$\frac{3.98}{145} = 0.028$$

the "sodium hydroxide factor" is found to be 0.99 (fig. 9).

The rate of reaction at the beginning of the second minute is therefore $0.35 \times 34.1 \times 0.43 \times 1.13 \times 0.877 \times 0.99 = 4.80$ cubic meters per minute.

The calculation of heat of reaction, heat losses, etc., for the second minute are made in the same way as for the first minute, and the whole computation is repeated for as many intervals as necessary during the run. In order to obtain a complete solution of the problem it is necessary to take account at all times of the temperature, previous yield of hydrogen, amount of sodium hydroxide present, amount of ferrosilicon present, and the amount of water present; in order to obtain these figures it is also necessary to determine for each interval the concentration of the solution, the vapor pressure of the solution, the water evaporated, the water added, the heat produced by the reaction, the heat lost by evaporation, radiation, and convection, the heat capacity of the generator and its contents, the "surface factor," the "concentration factor," the "sodium hydroxide factor," and the "temperature factor."

The volume of gas evolved, found by the solution of the problem in the manner indicated, is the volume which the gas would occupy at 0° C. and 760 millimeters if all water vapor were removed. The volume of gas leaving the generator and the volume leaving the condenser at any temperature may, of course, be calculated in the usual manner for correcting gas volume.

By multiplying the amount of ferrosilicon which has been added to the generator by the "surface factor" we may also determine the amount of unattacked ferrosilicon in the generator at any time.

All of the above quantities have been computed, for the case assumed for 1-minute intervals up to 31 minutes and for 5-minute intervals thereafter. The simultaneous values of the more important variables are shown in figure 16. Starting with a relatively large amount of ferrosilicon and a small amount of solution in the generator, the temperature rises very rapidly to 90°, the rate of gas evolution increasing by more than 50 per cent. Fresh solution is introduced to keep the temperature constant, and the rate falls off as the ferrosilicon is used up. As soon as the ferrosilicon feed is started, the rate of evolution begins to pick up.

Conditions then remain practically static until all the solution is introduced and water has to be used for cooling. This immediately dilutes the solution, making the rate of reaction per gram of material progressively slower. Ferrosilicon consequently accumulates gradually, the decrease in reaction from one cause almost exactly balancing the increase from the other. The more dilute solution has a greater vapor pressure and the total volume of hydrogen and steam leaving the generator increases considerably in consequence.

When the solution has been diluted to a concentration of 20 per cent, the addition of water is stopped. The temperature immediately begins to increase, the rate of reaction also increases, and ferrosilicon is consumed more rapidly than it is added. The temperature continues to rise until the vapor pressure is so high that the heat of vaporization of the water evaporated, together with the heat loss from the surface of the generator, balances the heat of reaction. The excess of ferrosilicon is quickly used up and the rate of consumption of silicon once more falls to approximately the rate of addition. If the rate of reaction per gram of ferrosilicon were constant the total rate of reaction would quickly become exactly equal to the rate of addition of ferrosilicon. There is, however, a continual change in the rate of reaction per gram caused by two factors—(1) the exhaustion of the sodium hydroxide tending to decrease the rate and (2) the gradual concentration of the solution as water is evaporated. Since the thermal equilibrium requires a constant vapor pressure, the temperature must rise as the solution becomes more concentrated, and this factor tends to cause a considerable increase of the rate of reaction per gram. The temperature increase is not quite sufficient to counterbalance the first effect and ferrosilicon again accumulates while the rate of evolution falls off slightly. When the ferrosilicon is all added, it is quickly exhausted and the evolution of gas drops to a very low rate. Eight minutes after the addition of ferrosilicon stops, only half a per cent of the 363 kilograms introduced into the generator remain unacted upon.

2. *Generator problem No. 2.*—Figure 17 represents the rate of evolution (curve *a*) and total yield (curve *b*) from the same amount of ferrosilicon and the same amount of sodium hydroxide, under the same weather conditions as assumed in problem 1 but with different conditions of operation. It is here assumed that enough water is added to the alkali in the mixing tank to make a 20 per cent solution, all of which is run into the generator at the start. The ferrosilicon feed is then started at the uniform rate of 15 pounds per minute. No water is added during the run. Under these conditions nearly 15 minutes are required to raise the temperature to a point at which the reaction goes on vigorously. By this time a large amount of ferrosilicon has accumulated and the rate of reaction becomes excessive.

Two additional curves representing the rate during the initial stages of generation with different methods of operation are shown. Curve *c* represents the result of operating under the same conditions as those represented by *a* except that only one-fourth of the solution is run into the generator at the start. Curve *d* represents the result of starting the run with 150 pounds of ferrosilicon and one-quarter of the solution in the generator; no more ferrosilicon is added up to the point shown.

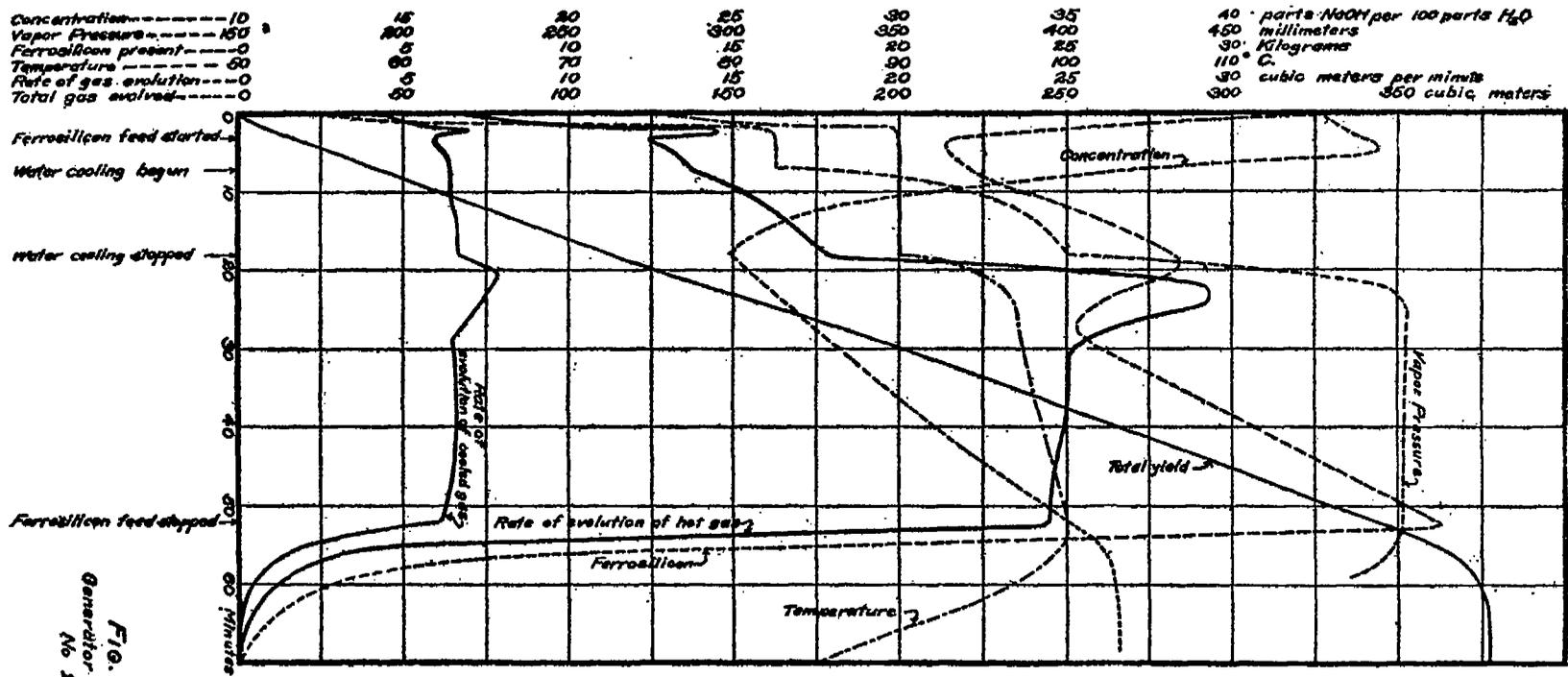


Fig. 16
Generator Problem
No. 1.

3. *Accuracy and significance of calculations regarding generator operation.*—The number of variables entering into such computations as those given above is so great and the data used in some cases so unsatisfactory that the results can not be regarded as possessing a high degree of absolute accuracy. This is particularly true in the case of the calculations concerning temperature changes in the generator. Thus in problem 1 the time required to raise the temperature of the generator to 90° C. is computed to be about three minutes. It would not be at all surprising if the time required in practice were found to be two minutes or five minutes. The data are hardly less useful on that account, however, since they enable one to compute with a considerable degree of accuracy the relative effect of the more important possible variations in generator operation and indicate with certainty the direction and order of magnitude of almost any change in the conditions or methods of generation.

In the first example given it is readily apparent that the low rate of evolution between the fourth and twelfth minutes could have been largely avoided by allowing the temperature to

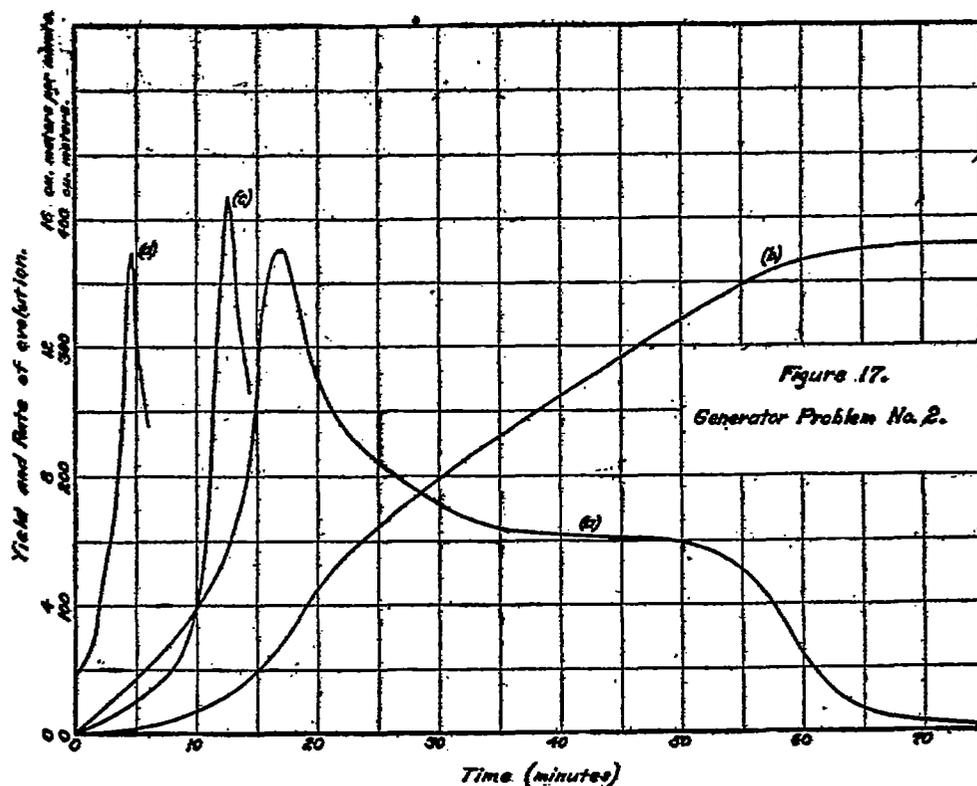


Figure 17.
Generator Problem No. 2.

increase further before adding water, and that the peak rate at about 20 minutes would have been avoided by the same procedure. This peak could also have been avoided by gradually decreasing the amount of cooling water instead of cutting off the supply suddenly.

F. CONCLUSIONS FROM THEORETICAL GENERATOR RUNS.

In spite of the many conditions affecting the rate of reaction of a given amount of ferrosilicon, the rate of gas evolution during the the major part of the generator run is primarily a function of the rate of feed of ferrosilicon. Whatever the conditions of temperature and concentration of solution, provided they are reasonably constant, and whatever the composition and fineness of the ferrosilicon, if the ferrosilicon feed is regular the material will accumulate in the generator until the amount of reacting surface is such that the rate of solution will closely approximate the rate of addition. Whether the rate of solution is greater or less than the rate of addition of material depends upon whether conditions are changing to make the rate of reaction per unit weight of ferrosilicon more or less rapid. In choosing conditions it is necessary

to determine: (1) That equilibrium will be quickly reached without generating gas at an excessive rate; (2) that there will be no sudden variations of generator conditions, particularly of temperature, which will greatly disturb the established equilibrium; and (3) that the material in the generator after the ferrosilicon is all added may be quickly and completely exhausted.

1. *Temperature control during generation.*—The first requirement of successful operation is that the temperature of the generator be quickly raised at the beginning of the run to the point at which equilibrium is to be established, and that this be done without accumulating a large surplus of ferrosilicon in the generator. The ideal condition is of course to adjust conditions so that when the temperature reaches the desired point the amount of ferrosilicon in the generator will be just sufficient to produce hydrogen at the average rate for the run.

If the generator temperature is to be increased to the desired point only by the heat of solution of sodium hydroxide and the heat of reaction with ferrosilicon it will probably be best to start with as concentrated a solution as can be quickly prepared and to use only a part of the solution with a comparatively large amount of ferrosilicon until the temperature reaches that at which it is desired to establish equilibrium. The ferrosilicon feed may then be started and more solution and water added as required to keep the temperature at the desired point. The temperature chosen for equilibrium should be determined by the following considerations:

(a) It is desirable to have the rate of reaction per unit weight of ferrosilicon as rapid as possible at the end of the run in order to avoid waste of time and material.

(b) The rate of reaction per unit weight of ferrosilicon at the end of the run can be made a maximum for a solution of given concentration by permitting the temperature to rise until thermal equilibrium is established between the heat of reaction on the one hand and the heat of vaporization and other heat losses on the other.

(c) The rate of reaction per gram is increased by increasing the concentration of the solution, but the allowable change in this direction is strictly limited by the fact that concentrated solutions containing much dissolved silicon become very viscous. It is probable that to utilize the materials economically the solution at the end of the reaction should never contain more than 33 parts of sodium hydroxide per 100 parts of water (a 25 per cent solution). Twenty-five parts of sodium hydroxide per hundred of water (i. e., a 20 per cent solution) would be a safer limit.

(d) The temperature must be kept from changing rapidly at any time after equilibrium is established. This is most readily accomplished by keeping it nearly uniform, and in order to fulfill the other requirements this working temperature must be slightly below the temperature at the end of the run.

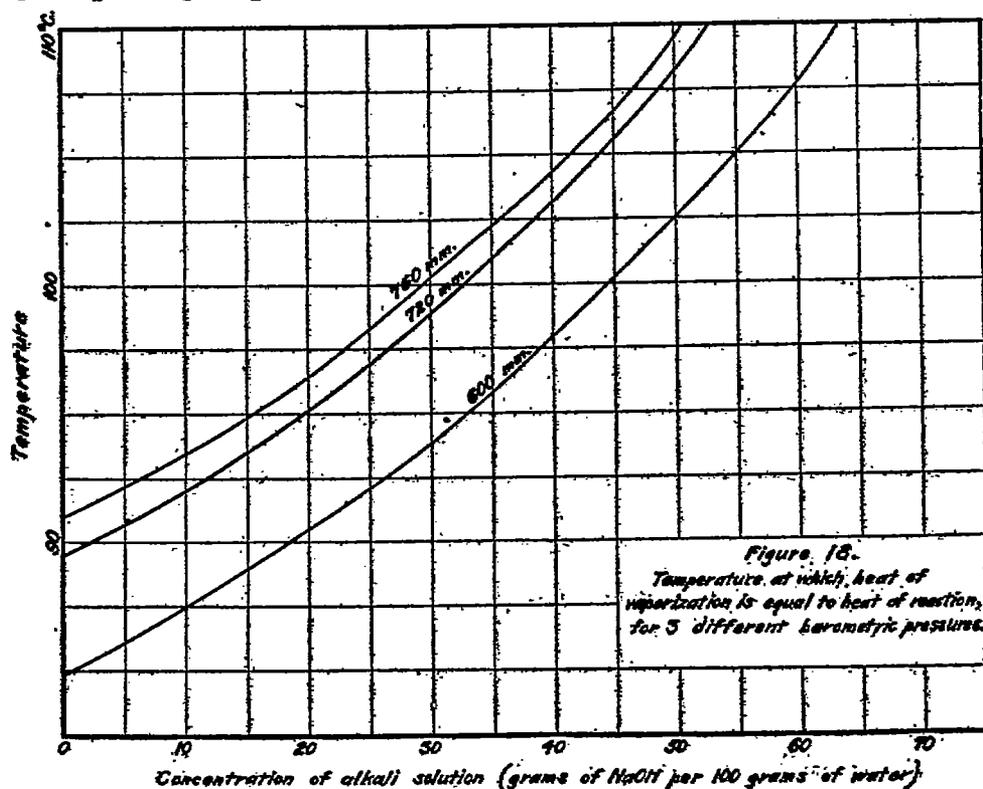
The use of some aluminum powder will permit a much more rapid heating of the generator than can be accomplished by the use of ferrosilicon alone, especially when at fairly low temperatures; and this preliminary use of aluminum will probably make it much easier to avoid excessive rates of reaction after the operating temperature is reached. In case aluminum is used, it will be far more economical and probably as satisfactory in every way to start with a fraction of the solution than to heat it all up at once. It will also be an advantage to introduce a considerable amount of ferrosilicon at the very start in order to secure a greater proportion of the necessary amount of heat from this material as the temperature rises. It is apparent from figure 16 that only two or three minutes are required to heat up the generator from 75° C. with ferrosilicon alone. Consequently it seems unnecessary to use more aluminum than is required to produce this temperature.

From data supplied by the Aluminum Co. of America it appears that about 1 gram of grained aluminum will raise the temperature of 1 gallon (3.8 kilograms) of solution 1° C.

A satisfactory result could probably be obtained by noting the temperature of the generator at the start and introducing 1 kilogram of aluminum per 100 gallons (or 380 kilograms) of solution for every 10° below 75° C. together with the amount of ferrosilicon which would be introduced if the temperature were already 75°. The amount of this initial charge will be discussed in the second section following.

2. *Choice of equilibrium temperature.*—Figure 18 shows the temperatures at which the heat of vaporization of the water carried away from solutions of various concentrations will be equal to the heat of reaction. These are the maximum temperatures beyond which the generator temperature could not rise if there were no heat losses other than through evaporation. On a still, hot day these temperatures will be approached closely if no cooling water is used. In very cold weather, and especially when a strong wind is blowing, the maximum temperature obtainable will be several degrees lower.

The temperature of the generator should be allowed to rise at the beginning of the run to within 2° or 3° of the maximum temperature possible for the solution of the concentration desired at the end of the run. The temperature should be kept at this point by means of the water spray until the amount of water required is very small. The water should then be turned off entirely and the temperature allowed to rise gradually, as it will do. If this point is reached before the run is half over and the discharged sludge is very viscous, a lower operating temperature should be chosen for the next run. If water cooling is required up to the very end of the run, a higher operating temperature should be maintained.



3. *Initial charge of ferrosilicon.*—As already pointed out, the initial charge of ferrosilicon should be such that when the generator temperature reaches the desired equilibrium value the rate of reaction will be the desired average rate for the run. In the case assumed in problem 1 about 12 kilograms of ferrosilicon, containing about 70 per cent silicon, was consumed in raising the temperature of the generator from 75° to 90°. The temperature should have been raised to about 95° to avoid the irregularities in rate which resulted from too low a temperature. The amount of silicon required to increase the temperature of 100 gallons of solution to the operating temperature is therefore about

$$\frac{12 \times 0.70 \times 20 \times 3.8}{15 \times 4.11} = 10.5 \text{ kilograms.}$$

The weight of ferrosilicon required is found by dividing 10.5 by the per cent of silicon contained. The generators in most common use are designed to deliver 12,000 cubic feet per hour, equal to 5.7 cubic meters per minute. In addition to the amount consumed in raising the

temperature, there should be enough material to produce hydrogen at the rate of 5.7 cubic meters per minute under operating conditions. Thus for the 70 per cent ferrosilicon used in problem 1 the initial charge should consist of about

$$\frac{10.5}{0.70} + \frac{5.7}{0.35 \times 0.83 \times 1.13} = 32 \text{ kilograms.}$$

The numbers 0.35, 0.83, and 1.13 occurring in the denominator of the second fraction are the initial rate of reaction in 20 per cent solution at 100°, the temperature factor, and the concentration factor, respectively.

If 88 per cent ferrosilicon ground to pass a 100-mesh sieve (fig. 5) were to be used, the initial charge should be about

$$\frac{10.5}{0.88} + \frac{5.7}{0.72 \times 0.83 \times 1.13} = 22 \text{ kilograms.}$$

If 32 kilograms of this material were used, the rate of evolution when the working temperature was reached would be about double the desired rate.

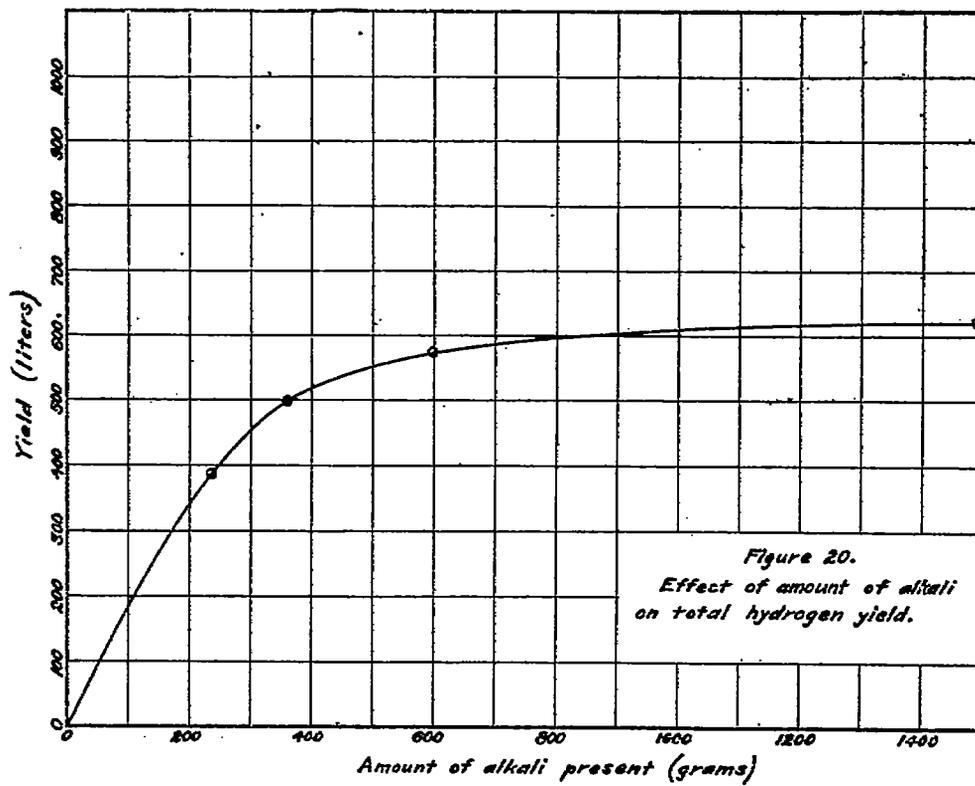
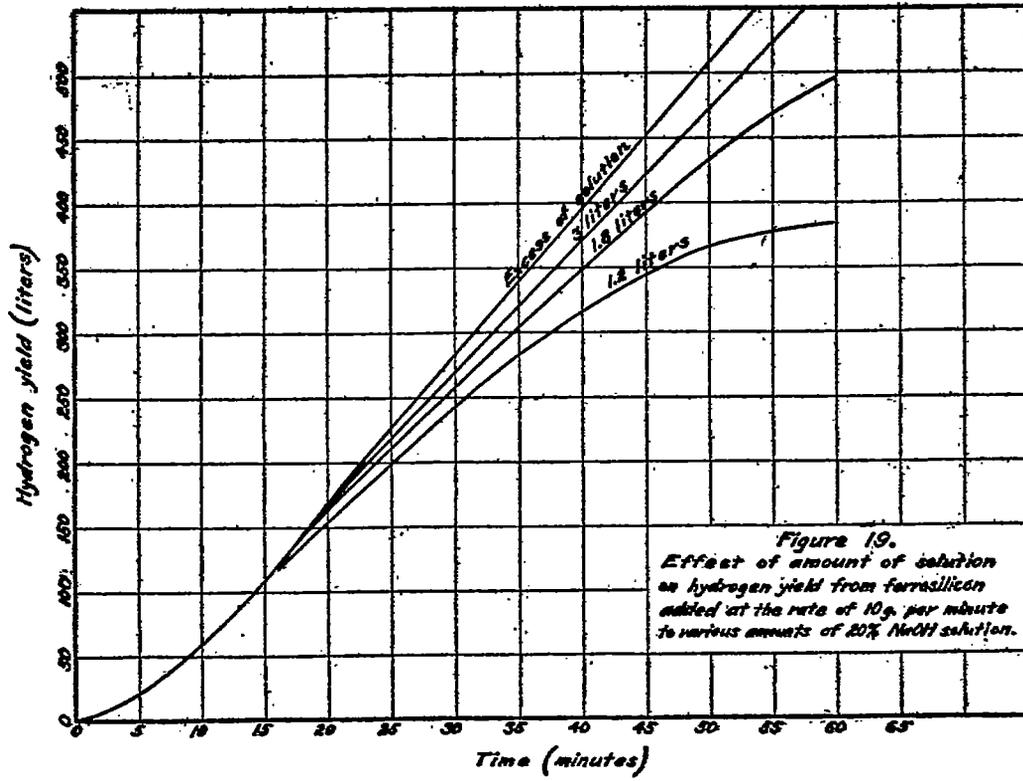
4. *Composition and fineness of ferrosilicon.*—If the best conditions of temperature control and generator operation indicated above are adhered to, the relative advantage of using ferrosilicon having different rates of reaction because of differences in composition or fineness is easily determined. If the temperature is fairly high, it is only necessary to add, at the start, the amount of material determined in accordance with the principles discussed in the last section. The temperature will then quickly rise to the desired value, the time wasted with the more slowly reacting material being practically negligible. If the temperature is very low, however, it can not be quickly raised with a slowly reacting material except by introducing so large an amount that the rate of reaction becomes excessive when the generator once gets hot. In some cases it might be impossible to produce sufficient reaction with low grade material to balance surface heat losses; it would then be impossible to operate the generator at all. If, however, aluminum is used, as recommended above, there is little advantage, so far as the initial stages of generation are concerned, in using a high grade or finely powdered material.

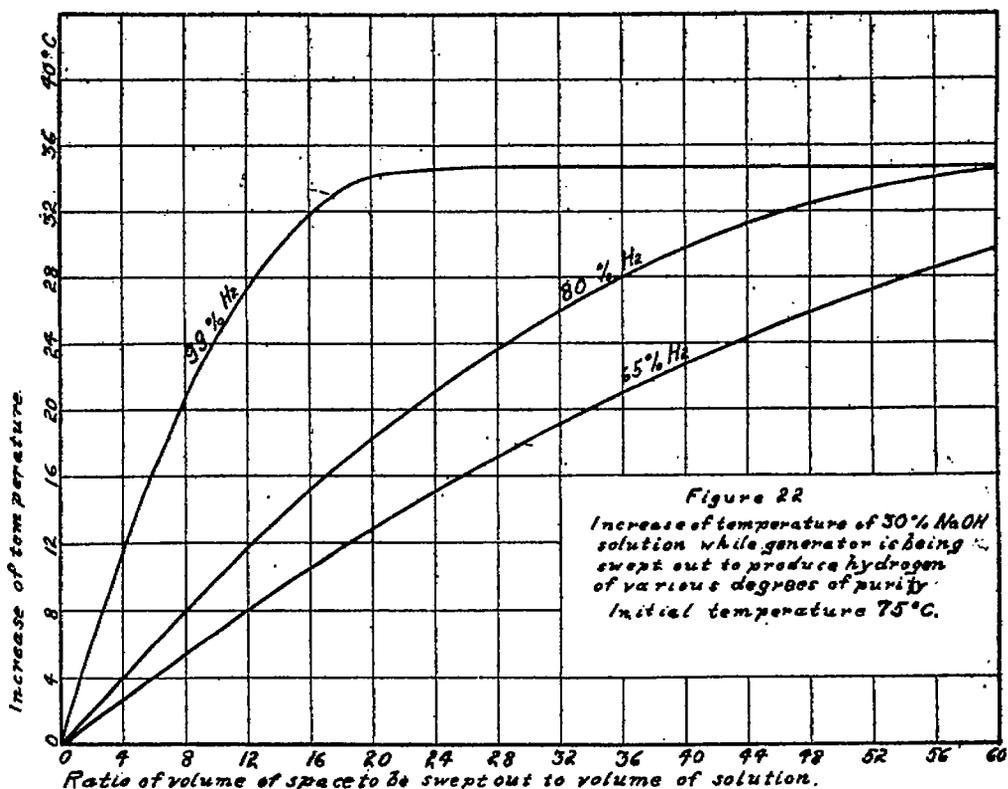
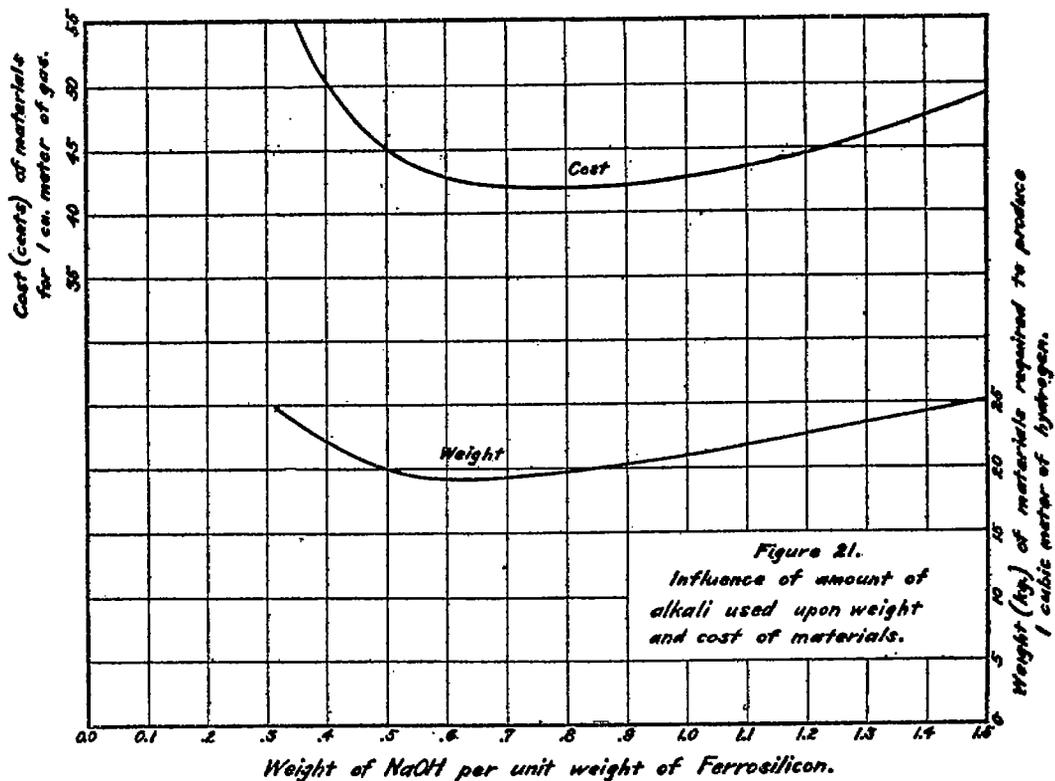
When once the reaction is proceeding at the desired rate, and the temperature and rate of addition of ferrosilicon are kept constant, it is obvious that generation will proceed at the same rate for any material until all the ferrosilicon has been fed into the generator. The amount of ferrosilicon present is then inversely proportional to the rate of reaction per gram of material, and at whatever time the run is stopped the amount of material wasted in the two cases is in this same ratio. The amount wasted at the end of the reaction is not large if a reasonable time is allowed for the reaction to cease. The material assumed for problem 1 was about as slow acting as there will probably be occasion to use; the amount unattacked when the addition of material ceased was about 10 per cent; five minutes later it was about 2 per cent, and in another five minutes it had fallen to half of 1 per cent. It is clear, therefore, that even coarse, low-grade material does not unduly prolong the period for reasonably complete reaction.

5. *Amount of sodium hydroxide.*—Figure 19 shows the total yield of hydrogen computed from the experimental data shown in figure 9, for the same amount of 88 per cent ferrosilicon added at the same constant rate to four different amounts of 20 per cent sodium hydroxide solution during a period of one hour, the temperature and concentration being assumed constant during the interval. The hydrogen yield during 60 minutes under these conditions is plotted against amount of alkali in figure 20.

From the data of these curves were computed the total weight and the total cost of the ferrosilicon and sodium hydroxide (assumed to be 12.5 and 6 cents per pound, respectively) to produce 1 cubic meter of gas.

The results are given in figure 21, from which it appears that the greatest economy will be obtained by using about seven-tenths as much sodium hydroxide as ferrosilicon of this composition, or about eight-tenths as much sodium hydroxide as silicon present in the material.

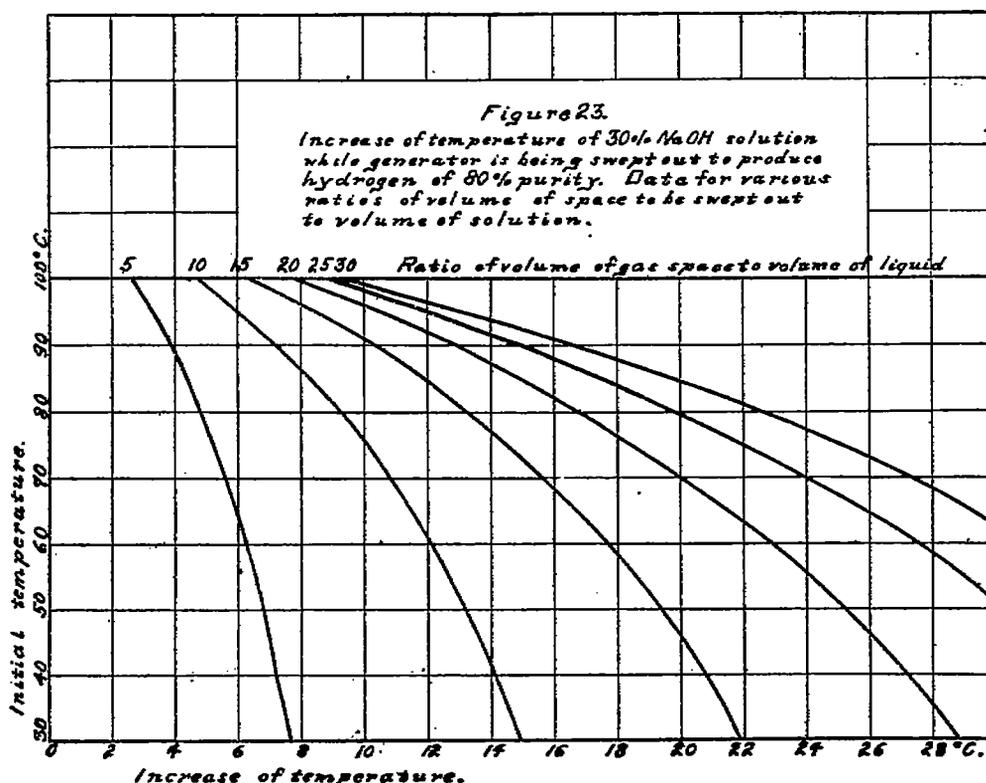




There is, however, but little waste in using equal weights of ferrosilicon and sodium hydroxide, and such a practice would decrease the danger of obtaining very viscous solutions at the end of the run. On the other hand, it costs more to produce a given volume of hydrogen when too little sodium hydroxide is used only because ferrosilicon remains unacted upon at the end of the run. It has already been pointed out that the amount of material wasted decreases very rapidly when generation is permitted to proceed for a short time after the material is added; hence when haste is not an important object greater economy could no doubt be secured by using a still smaller proportion of alkali than 7 parts to 10.

G. SWEEPING OUT THE GENERATOR.

The hydrogen first coming from the generator is, of course, contaminated with the air in the generator at the beginning of the run. Since it is undesirable to run this air into the balloon, the gas first produced should be allowed to escape into the atmosphere. The volume of hydrogen



which must be wasted before the desired purity is reached depends upon the volume of gas space to be swept out and is constant for a given generator and a given initial charge of solution. Since a definite amount of heat is produced when a definite mass of hydrogen is evolved, the easiest and most reliable way of determining when the desired volume of hydrogen has been liberated is to observe the rise of temperature of the solution.

In the following discussion of the temperature increase corresponding to various degrees of purity of hydrogen at the outlet of the generator it is assumed that the gases within the generator are uniformly mixed. This is a safe assumption, since the hydrogen is liberated uniformly, or nearly so, over the bottom of the generator and any settling of the air at the bottom without mixing is inconceivable. On the other hand, it is to be expected that the hydrogen will to a considerable extent displace the air without mixing. If there were no mixing at all, the volume of hydrogen required to sweep the air out completely would, of course, be equal to the volume of the gas space.

Assuming uniform mixing of the gas within the generator at all times, it may be shown that the ratio R of the volume of hydrogen evolved to the volume of the gas space into which it is liberated is given by the equation

$$R = \log_{10} \frac{1}{1 - \frac{a}{100}}$$

where a is the percentage of hydrogen in the generator.

From this equation and the thermochemical data already given it is possible to compute the rise of temperature of the generator and its contents when under any given set of conditions before a gas of a given purity is obtained.

In making the computation for the cases shown in figures 22 and 23 the following assumptions were made:

1. That there is perfect mixing of the gases within the generator.
2. That all the heat produced by the reaction goes to heat the solution or to evaporate water from the solution.
3. That the molecular volume of water vapor is equal to that of a perfect gas at the same temperature and pressure.
4. That normal barometric pressure (760 millimeters of mercury) exists.
5. That the effect of concentrating the solution through evaporation during the reaction is inappreciable.

The first two assumptions are on the side of safety and they will more than overbalance any probable errors in the opposite direction from an abnormally high barometric pressure or other cause. The hydrogen after a given temperature increase will therefore always be somewhat purer than is indicated by the figures 22 and 23.

Figure 22 shows the increase of temperature from an initial temperature of 75°, corresponding to the production of hydrogen of 65, 80, and 99 per cent purity for all ratios of volume of gas space to volume of solution up to 60. The curve for 65 per cent was constructed because this is about the lowest percentage of hydrogen which will not explode if ignited. It is common balloon practice to reject hydrogen of less than 80 per cent purity because of its low lifting power. This is therefore the purity which it is desirable to reach before allowing the gas to enter the balloon. The curve for 99 per cent purity is given as a matter of interest.

Figure 23 shows, for several ratios of gas space to volume of solution, the temperature increase necessary to produce hydrogen of 80 per cent purity when starting the generation at any temperature. Under the conditions recommended for operating the generators now in use, the space to be swept out is about 15 times the volume of the solution in the generator at the beginning of the run.

If a more dilute solution than 30 per cent is used, or if the barometric pressure is lower, a somewhat purer gas will be obtained for a given temperature increase than that indicated in the figures because of the cooling effect of increased evaporation.

APPENDIX.

SUGGESTIONS AND TENTATIVE OPERATING DIRECTIONS.

The following suggestions and operating directions are intended to summarize in a concise form the practical applications of the foregoing theory. From the nature and complexity of the problem it is not to be expected that the exact details specified will be the best in every case, but it is hoped that the principles already developed will enable the operators to quickly determine from field experience the points at which these directions are at fault and to make the necessary modifications at once. Following the specific directions are comments upon possible modifications.

1. *Purchase of material.*—(a) Ferrosilicon, if purchased on the basis of content of silicon, should contain not less than 75 per cent of that element. If purchased on the basis of yield of gas, it should evolve not less than 1.1 liters of dry hydrogen per gram measured at 0° C. and 760 millimeters pressure.

(b) The choice of ferrosilicon containing more than 80 per cent of silicon should be governed by total cost per unit volume of hydrogen obtainable.

(c) The ferrosilicon should be ground at least fine enough to pass a 16-mesh sieve. It is some advantage to have it finer than this, but the advantage probably would not justify an increased cost of more than 5–10 per cent for grinding.

(d) Sodium hydroxide should be purchased on the basis of content of sodium hydroxide allowing nothing for sodium carbonate, which is of no value.

2. *Computation of generator charges.*—For each lot of material purchased the following points should be determined once for all, either by test or by computation, using the data given in this report with such modifications as experience may prove desirable:

(a) Determine the total gas yield per unit weight of ferrosilicon.

(b) Determine the initial rate of reaction per unit weight of ferrosilicon, for the conditions under which equilibrium is to be established in the generator.

(c) Compute the total generator charge to be used for a single run, from the volume of gas desired and the total yield obtainable from the material.

(d) Compute the rate of ferrosilicon feed, from the total yield per unit weight of material and the capacity of the washer-cooler system (or the danger of foaming if that proves to be the limiting factor), on the assumption that the rate of consumption of material will equal the rate of feed.

(e) Compute the initial charge, in the manner described in section E-3 of this report.

(f) Compute the charge of sodium hydroxide. The weight of sodium hydroxide used should be about 80 per cent of the weight of silicon in the ferrosilicon charge. Probably a good rule would be to use whole packages if possible, always using a weight of sodium hydroxide between 80 per cent and 100 per cent of the weight of silicon.

(g) Compute the amount of water required to make a 30 per cent solution with the sodium hydroxide charge specified.

(h) From the data of figure 22, compute for the operating conditions to be used the temperature rise corresponding to a purity of hydrogen of 80 per cent.

3. *Operating directions.*—(a) Introduce into the mixing tank the amount of water specified (2g), start the stirring machinery, and add the amount of sodium hydroxide specified (2f).

(b) Fill the ferrosilicon hopper, but do not start the feed.

(c) When solution of the alkali is complete, run 100 gallons (or 380 liters) of the solution into the generator. Read the temperature. If the solution is very cold, and especially if there is reason for haste, add at one time 1 kilogram (or 2.5 pounds) of grained aluminum for every 10 degrees below 75° C., and the specified initial charge of ferrosilicon (2e).

(d) Let hydrogen run to waste until the temperature has risen the predetermined amount (2h), then pass into the storage tank or the balloon.

(e) Watch the temperature of the generator carefully. When it reaches 95°, start the silicon feed at the specified rate (2d) and start to run in additional solution from the mixing tank and, if necessary, cooling water as fast as required to keep the temperature constant at 95°. Introduce the solution as rapidly as possible without lowering the temperature; but introduce water before the addition of all the solution only if it is necessary to keep the temperature from rising.

(f) Put more ferrosilicon in the hopper before the material first introduced is all exhausted. Continue to do so until the specified charge (2c) is all introduced.

(g) When the amount of cooling water required to keep the temperature constant becomes very small (it will never become zero), stop it entirely. If the temperature then rises more rapidly than one or two-tenths of a degree per minute, begin cooling again.

(h) Record any indications of irregular evolution of gas or low yield. Note and record the condition of the sludge when discharged, whether it appears sticky or doughlike or whether the grains of material appear distinct and easily separable.

4. *Comments upon directions given.*—1a. It is recommended that, following the French practice, the quality of ferrosilicon be specified on the basis of hydrogen yield. There are two reasons for this: (1) The hydrogen yield is much more easily and quickly determined than the percentage of silicon; and (2) the hydrogen yield is the property of immediate value, and it may not always be proportional to the silicon content as determined by analysis. For example, a mixture of sand and ferrosilicon containing 91 per cent of silicon element, so proportioned that the free and combined silicon forms 85 per cent of the mixture, will yield only 92 per cent as much hydrogen as ferrosilicon of uniform composition containing 85 per cent of silicon element. Yet both samples would show the same percentage of silicon if analyzed by the usual methods. On the other hand, some hydrogen is formed from aluminum and perhaps other impurities in the ferrosilicon.

The following method of determining yield of hydrogen is recommended: The apparatus required is shown in figure 1, in which *A* is a 500 cc. flask of pyrex glass sufficiently heavy to stand evacuation. This flask is connected as shown to the bottle *B* in which the evolved gas is collected and the bottle *C* in which its volume is determined by measuring with the graduated cylinder *D* the volume of water displaced. The stopper of *A* carries a dropping funnel *E*, and a connection to a source of reduced pressure and to the mercury manometer *F*. Provision is made for connecting bottle *G* to a source of pressure or of suction, or for opening it to the atmosphere at will.

A 2-gram sample of the ferrosilicon is weighed into the flask *A*, 100 cc. of water is added, the flask is opened to the vacuum line, and the contents boiled until all the air has been expelled by water vapor. The vacuum is then shut off, 100 cc. of 40 per cent sodium hydroxide solution is placed in the dropping funnel, and the alkali is let into *A* drop by drop until the evolution of hydrogen begins. As soon as the pressure in *A* approaches atmospheric, as shown by the mercury manometer, the stopcock into *B* is opened and the evolved gas passes into *B*, displacing the water into *G*, which is open to the air. The addition of the alkali to *A* is now continued carefully, the temperature being kept near the boiling point at all times. When all the alkali has been added and the reaction slows down, the heat is increased and the solution allowed to boil for one hour. *A* is then filled with water through the dropping funnel, the gas is run into *C*, and the amount of water displaced from *C* measured. When all the gas has been forced into *C*, it is brought to atmospheric pressure by raising the measuring vessel until the water stands at the same level as in *C*, the end of the delivery tube being kept under water at all times. The temperature of the displaced water is determined and the volume of the gas corrected to standard conditions of temperature and pressure.

1c. If the ferrosilicon is to be used under conditions of known cold and windy and variable weather, particularly at a high altitude, it will probably be best to have the material finely ground in order to permit easier temperature control at the beginning of the run. If foaming

causes trouble, but little difficulty is experienced in getting up to the desired operating temperature, it may prove desirable to use a coarse material.

2c. If the generator is to be used to fill a balloon of given size without the aid of a nurse balloon or relief holder, an integral number of charges should be used to fill the balloon, the weight of each charge being computed from the total yield per unit weight of ferrosilicon. If the generator is to be operated to keep up a supply in a holder, the amount of a charge should be as large as the capacity of the generator will allow, using an integral number of packages of materials. A considerable saving both of time and material can be gained by increasing the charge and correspondingly increasing the time required to exhaust it. If the reduced amount of solution recommended in this report is used, it may be possible to very materially increase the charge in this way.

2d. The permissible rate of ferrosilicon feed for a generator and condenser of a given size and form should be determined once for all. Unless there is trouble from foaming, the maximum permissible rate is that above which the outlet gas shows a temperature appreciably higher than that of the condenser water or contains sodium hydroxide spray.

2e. Some sort of device for determining the rate of evolution of gas is very desirable. A Venturi meter of the type used on the French machines is sufficiently accurate. If such a meter is attached, it is easy to determine whether the amount of initial charge is correct. When the temperature of the generator reaches the operating temperature, the feed is started at the full rate. If the rate of evolution of gas then decreases during the next few minutes while the temperature is kept constant, the initial charge was too large. If, on the other hand, the rate of evolution increases when the feed is started, the initial charge may advantageously be increased.

2f. When speed is of primary importance in the generation, there will be some advantage in increasing the amount of sodium hydroxide used. When, however, time is of little importance, economy can be gained by keeping the amount of sodium hydroxide at the minimum figure given. The amount of sodium hydroxide should probably never be much lower than this. If a pressure record of the rate of evolution is kept, it will give some indication of whether enough alkali is being used or not. If there is a rather sharp diminution in rate near the end of the run, with a constant or rising temperature, it is a pretty good indication that more sodium hydroxide would save time and perhaps money.

2g. If an excessive amount of time is required to get the sodium hydroxide into solution, and particularly if the temperature in the mixing tank passes through a maximum before solution is complete, the solution is being made too concentrated. If the alkali goes into solution promptly and there is difficulty in starting generation when the solution is run into the generator, the solution may advantageously be made more concentrated.

A 30 per cent solution is chosen rather arbitrarily as representing about the strongest solution which can be made up rapidly. At any rate, there is but little advantage from any standpoint in making a solution much stronger than this. When working at a high altitude, there is some advantage in having the solution somewhat more concentrated at all times during the run than when working at a low altitude, because the vapor pressure, and consequently the heat losses and the equilibrium temperature, are then nearer normal.

3c. The amount of solution introduced into the generator at the start is here chosen arbitrarily. It may be found preferable, in practice, to use more or less than this amount, and it may be found advantageous to change the amount for different weather conditions. When starting with a cold solution it should always be possible to economize upon the amount of aluminum necessary by reducing (within reasonable limits) the amount of solution used at the start, but it is probable that a very great reduction would result in considerable loss of time.

3e. The exact operating temperature, here somewhat arbitrarily chosen, must be fixed by experience. It can not be made as high as was formerly used without allowing the solutions to become very concentrated toward the end of the run, and this condition does not permit economy in the use of sodium hydroxide. The amount of sodium hydroxide to be used should be chosen without regard to this factor.

If it is then found necessary to add a considerable amount of water until the very end of the run in order to keep the temperature down, the operating temperature chosen is too low. If the amount of water required is very small early in the run and the discharged sludge is very viscous, the operating temperature is too high. Some difference in choice of operating temperature should probably be made for different weather conditions. These changes will have to be determined by experience. In general, it may be said that a high wind velocity has a greater effect than a low temperature or a low barometer.

It is of no great consequence whether cooling water and fresh solution are introduced together or not provided the solution is all introduced before the rate begins to fall off appreciably because of the exhaustion of the sodium hydroxide.

If there is any foaming over at any time during the run or if the gas leaves the washer at a temperature appreciably higher than that of the inlet water, the rate of feed of ferrosilicon is too high. The temperature of the outlet gas should be carefully watched. If it shows a sudden increase while the ferrosilicon feed is maintained at the usual rate, the fault is in the washer and should be remedied as soon as possible. In the meantime the rate of feed of ferrosilicon should be decreased enough to allow the gas to pass out well cooled, especially if the gas is being run directly into a balloon. If the gas is passing into a relief holder, thorough cooling is less essential.

3g. It may be preferable to specify the time at which the cooling water is to be shut off. This should be 10 or 15 minutes before the ferrosilicon is all fed into the generator in order (1) to allow the generator temperature to rise as much as possible, (2) to offset the effect of diminishing concentration of sodium hydroxide, and (3) to prevent waste of material at the end of the run.

3h. A permanent record of all generator runs and all indications of unsatisfactory operation should be of considerable value, at least until the method of operation is thoroughly standardized. The record will be particularly valuable if it can be accompanied by a record of the generator pressure.

REPORT No. 40.

PART II.

THE EFFECT OF THE PRESENCE OF SODIUM CARBONATE ON THE GENERATION OF HYDROGEN FROM FERROSILICON AND SODIUM HYDROXIDE.

By E. R. WEAVER and B. D. GORDON.

Introduction.—The purpose of the experimental work described in this report was to determine the allowable limit for sodium carbonate in sodium hydroxide that is to be used for the generation of hydrogen by the ferrosilicon method and the possible value of sodium carbonate for this purpose.

Method of study.—Solutions containing known amounts of sodium hydroxide and sodium carbonate were prepared. The solution to be investigated was transferred to a large flask connected through a water-cooled condenser to a gas meter. The flask was heated to constant temperature in a steam jacket and 25 grams of ferrosilicon were then added and the rate of hydrogen evolution and the total yield of hydrogen determined. The presence or absence of CO₂ in the evolved hydrogen was determined by bubbling this gas through a little barium hydroxide solution before it entered the meter.

In each of the experiments a 20 per cent sodium hydroxide solution, an equivalent solution of sodium carbonate, or a mixture of the two was used. The use of solutions of equivalent strength in all experiments was intended to make the results more directly comparable. Since sodium carbonate is more strongly hydrolyzed in a dilute than in a concentrated solution, it is apparent that (1) the carbon dioxide would be produced from a dilute solution if it is produced at all and (2) that sodium carbonate would prove of greater value, relative to an equivalent amount of sodium hydroxide, in a dilute solution than in a concentrated one. An equivalent strength of 20 per cent of sodium hydroxide was chosen for the experiments, because this concentration is about as low as it is practicable to use in the hydrogen generator. The ferrosilicon used in the several experiments was of the same composition and fineness, and all conditions of generation except the composition and amount of solution were made identical in all the experiments.

Results of experiments.—The results of representative experiments are given in the form of curves. Figure 1 shows a typical curve representing the evolution of hydrogen from ferrosilicon in a solution of pure sodium carbonate. The very much greater hydrolysis of sodium silicate than of sodium carbonate probably accounts for the peculiar shape of the curve.

Figures 2 and 3 represent the results of a series of experiments in each of which an excess of solution containing sodium hydroxide and sodium carbonate equivalent to 20 per cent of sodium hydroxide was allowed to react with the same amount of ferrosilicon. For comparative purposes another series of experiments was made with solutions containing the same amount of water and sodium hydroxide as the corresponding solution in the first series, but no sodium carbonate. It will be seen that the presence of sodium carbonate equivalent to as much as three times the sodium hydroxide present has very little effect either on the rate of evolution or the total amount of gas evolved in 30 minutes. It can be readily seen that sodium carbonate has even less effect upon the total production of gas from a field generator, because the rate of evolution during most of the time is a function of the rate of ferrosilicon feed only.

Figure 4 shows the results of several typical experiments. The composition of the solutions in the experiments represented by curves *A* and *C* were the same, but the amount of solution used with 25 grams of ferrosilicon was greater than should be used in practice in *A* and less than should be used in practice in *C*. Curves *B* and *D* represent, respectively, the evolution of hydrogen from the same amount of solution containing the same amount of sodium hydroxide as curves *A* and *C*, but no sodium carbonate. It is obvious that in experiments *A* and *C* the sodium carbonate, equivalent to 25 per cent of the total alkali present, has but little value. Curve *E* represents hydrogen evolution from a solution in which the sodium carbonate is equivalent to 75 per cent of the total alkali, and the total sodium hydroxide equivalent is about that found to be most favorable to economy in generator operation. Under these conditions, if under any, sodium carbonate should prove of value. A comparison with a solution containing the same amount of sodium hydroxide but no carbonate, represented by curve *F*, shows that the carbonate has but little value even under these circumstances.

Conclusion.—The reaction of sodium carbonate in solution with ferrosilicon probably depends entirely upon its hydrolysis which takes place according to the following equation:

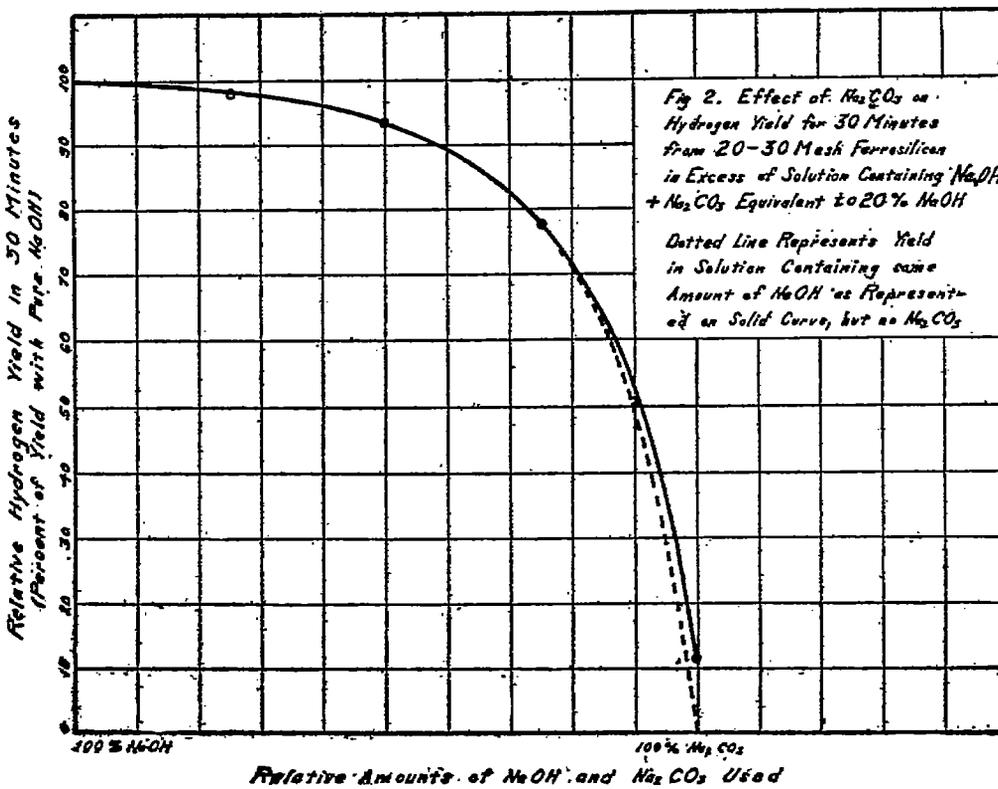
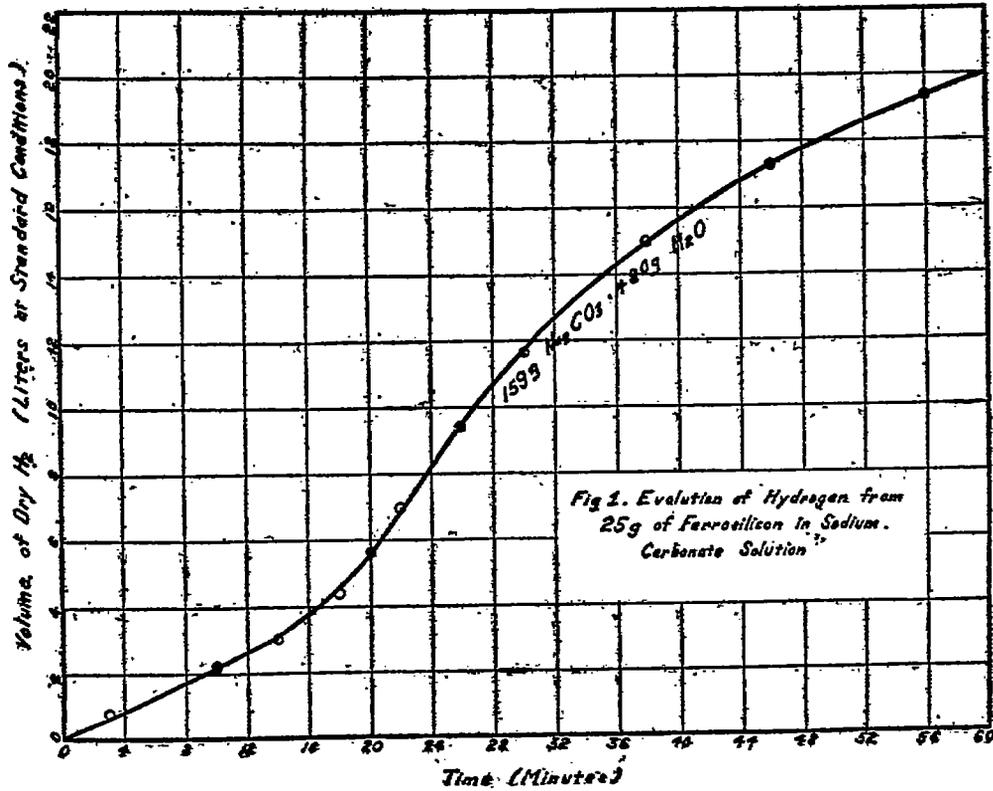


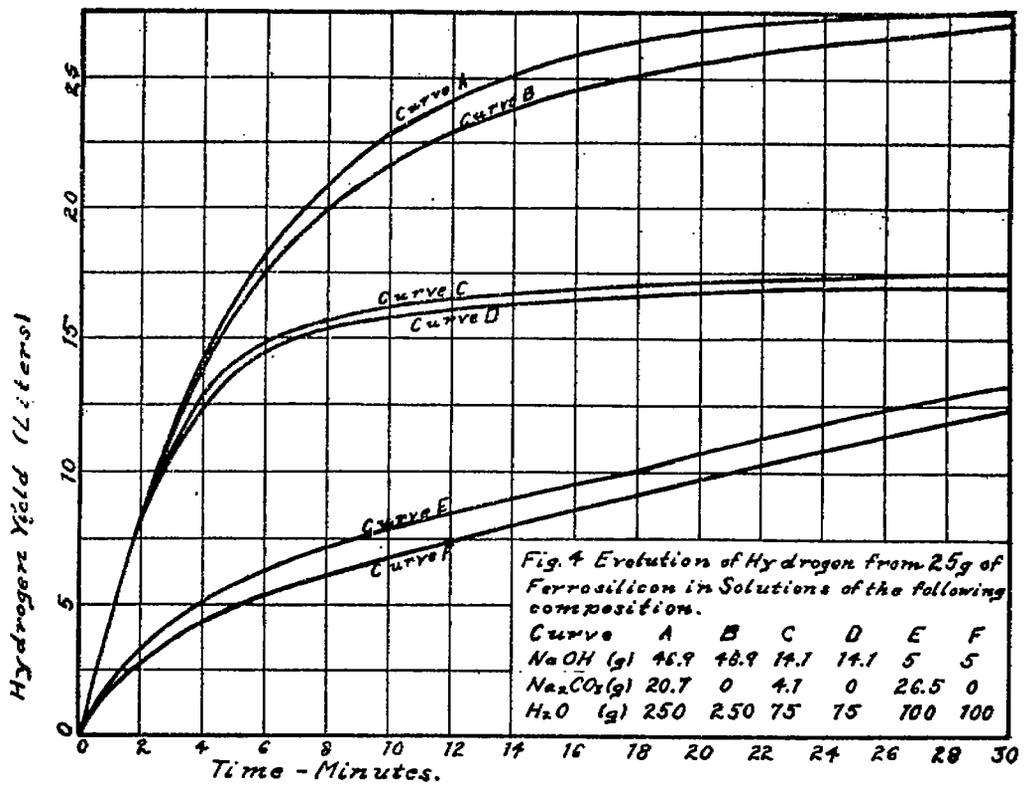
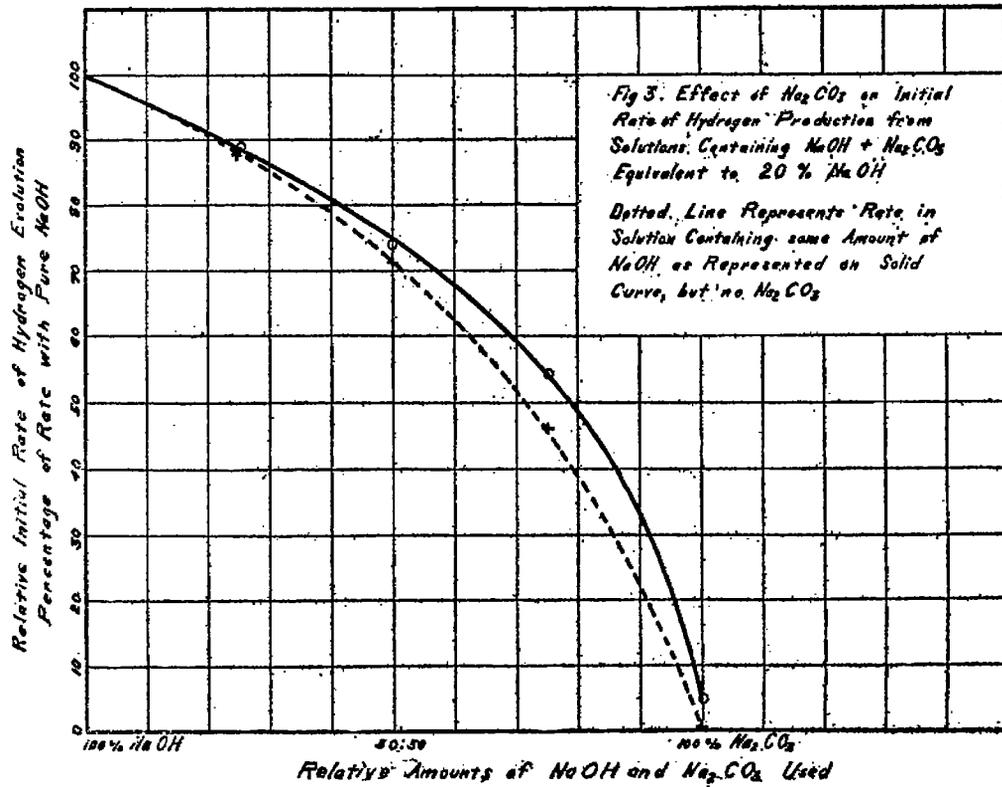
This reaction takes place to the extent of about 3 per cent in a 20 per cent solution. In the presence of sodium hydroxide or of any considerable quantity of sodium silicate which is much more strongly hydrolyzed than the carbonate, it is apparent from the law of mass action that the above reaction will be reversed and the sodium carbonate will have little or no value.

So far as its reaction with ferrosilicon is concerned, sodium carbonate, occurring in sodium hydroxide as an impurity, is an inert material and has no value whatever.

Since no carbon dioxide is formed from the reaction with ferrosilicon at any concentration of alkali in which we are interested, the presence of sodium carbonate is not harmful in any way.

Recommendation.—We recommend that sodium hydroxide for hydrogen generation be purchased on the basis of actual sodium hydroxide contained and that no allowance be made for carbonate. If this is done, there is no apparent reason why the amount of carbonate should be limited, except by the cost of transporting useless material.





REPORT No. 40.

PART III.

THE USE OF LIME IN THE GENERATION OF HYDROGEN BY THE USE OF FERROSILICON.

By B. D. GORDON.

1. PURPOSE AND SCOPE OF INVESTIGATION.

In the generation of hydrogen by the use of ferrosilicon and sodium hydroxide the silicon goes into solution as an alkali silicate, and hydrogen is produced from the water which enters into the reactions involved. Any other strong alkali used in place of sodium hydroxide will produce a similar reaction.

This paper describes an attempt to develop a method of using lime to replace some or all of the sodium hydroxide. Such a substitution would be desirable for the following reasons:

1. Lime is the cheapest of alkalis, usually costing only a small fraction of the cost of sodium hydroxide.

2. Lime is obtainable almost anywhere; it is produced in so many localities that high transportation costs may usually be avoided; and it is much easier, on account of the relatively inexpensive apparatus involved, to expand the production of lime to meet an unusual demand. Sodium hydroxide is one of the important chemicals of which there is always a more or less serious shortage in war time.

3. Sodium silicate, the end product of the reaction involved in the production of hydrogen, is quite soluble and is strongly dissociated by water. It is very injurious to both animal and vegetable life and may become a serious nuisance in the neighborhood of the generator if not properly disposed of. Calcium silicate, on the other hand, is an insoluble mineral which has no dangerous properties of any kind.

4. The physical and chemical properties of lime render it much easier to transport and handle than sodium hydroxide.

The three following possible methods of using lime were considered:

1. To determine whether it is practicable to substitute lime for sodium hydroxide directly in the production of hydrogen.

2. To determine whether it is feasible to recover sodium hydroxide from the sludge remaining after the generation of hydrogen from ferrosilicon and sodium hydroxide.

3. To determine the practicability of using a mixture of lime and sodium carbonate instead of sodium hydroxide.

2. THE DIRECT USE OF LIME IN THE GENERATOR.

Sodium hydroxide and ferrosilicon react according to the following equation:



Similarly we might expect calcium hydroxide (slaked lime) to react according to the following equation:



When, however, a calcium hydroxide solution containing some of the undissolved solid (milk of lime) was heated with ferrosilicon in a steam jacket for half an hour no appreciable quantity of hydrogen was produced. This result is easily explained when it is remembered

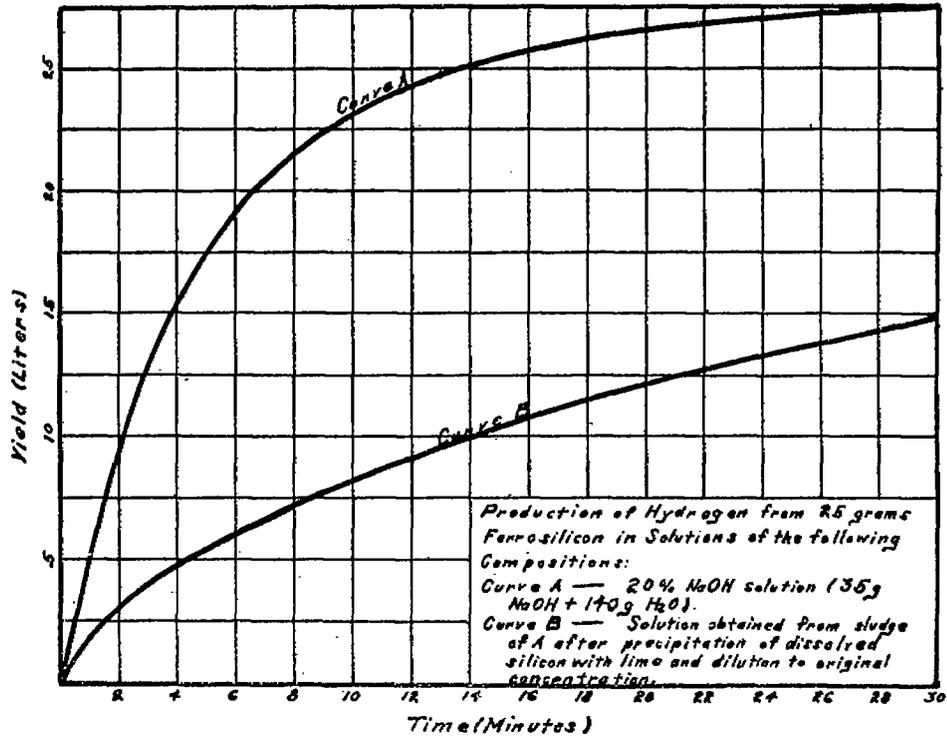


FIG. 1.

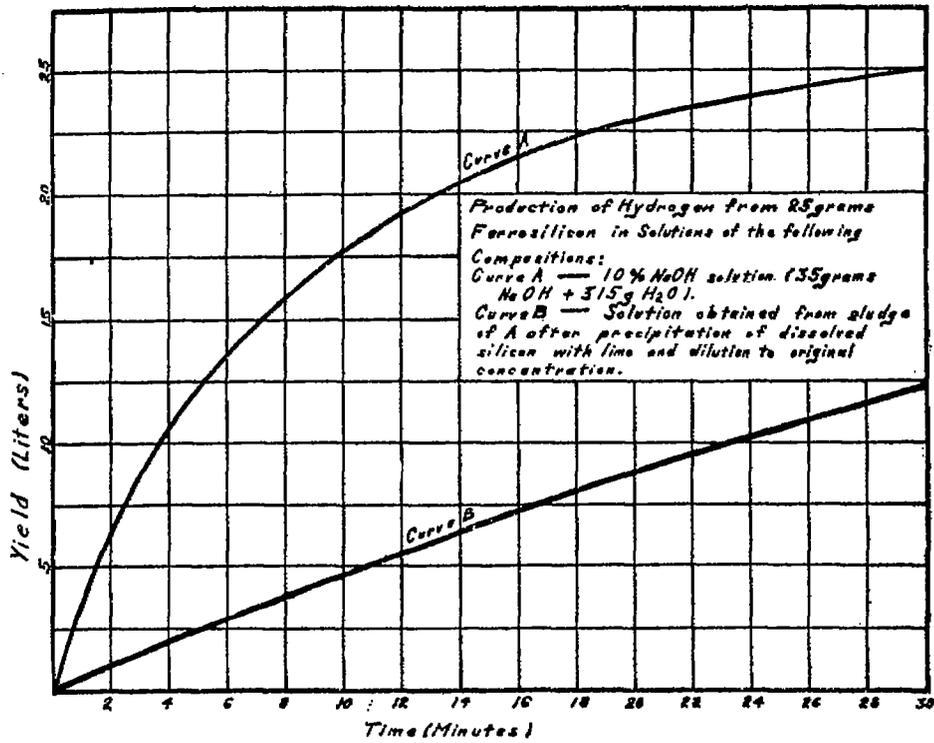


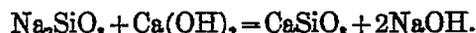
FIG. 2.

that the rate of reaction between ferrosilicon and sodium hydroxide is too slow to be of practical value when less than a 10 per cent solution of the alkali is used and that a saturated solution of lime at 100° contains only about 0.12 per cent of the solid.

Lime can not, therefore, be used directly as a substitute for sodium hydroxide in the process.

3. RECOVERY OF SODIUM HYDROXIDE FROM GENERATOR SLUDGE.

Calcium silicate is less soluble than calcium hydroxide. We would therefore expect to be able to recover sodium hydroxide from the sodium-silicate sludge with the formation of the insoluble calcium silicate according to the following reaction:



The effective amount of sodium hydroxide which can be recovered in this way was determined in the following manner:

A weighed amount, 25 grams, of ferrosilicon was permitted to react with a 20 per cent sodium-hydroxide solution in the proportions and under the conditions used in a hydrogen generator. When the reaction was complete, the water lost by evaporation was replaced, a sufficient quantity of lime to react with all the sodium silicate was added; the temperature of the reaction flask was brought back to the temperature at the beginning of the first reaction, and 25 grams of ferrosilicon was again added. Figure 1 represents the evolution of hydrogen for a period of 30 minutes under the two conditions. Figure 2 represents similar data for a 10 per cent solution. It will be seen that in each case only about half as much hydrogen is obtained in half an hour from the recovered sludge as from the original solution, and that the falling off in the rate at the beginning of the reaction is even more serious.

It is obvious that much less sodium hydroxide is present in solution after precipitation than was present in the original solution. This may be due to the absorption of the hydroxide by the colloidal silica and calcium silicates which form a jellylike mass.

To obtain further evidence on this point, a sodium silicate sludge formed under generator conditions was precipitated with an excess of milk of lime, filtered with the aid of suction, and the filtrate titrated to determine the amount of sodium hydroxide recovered. The precipitate was then boiled for four hours with water and again filtered and the filtrate titrated. By the first filtration 38.9 per cent of the original alkali was recovered, and 13.3 per cent additional was obtained by the first digestion and washing. Only negligible amounts were obtained by subsequent washing. It thus appears that about 50 per cent of the sodium hydroxide, or sodium silicate unacted upon, is permanently included in the precipitate. It requires very careful treatment to recover even 50 per cent of the original alkali.

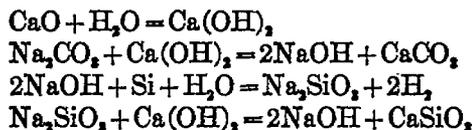
The precipitate of calcium silicate is so voluminous that practically no separation of precipitate and solution occurs on standing, and in order to recover the alkali commercially it would be necessary to use a filter press. If sludge were produced at one place regularly in large quantities, it would unquestionably be economical to recover as much sodium hydroxide as possible by the installation and use of a filter press. The ferrosilicon method for the production of hydrogen is practically never used under such conditions, however; its principal advantages are portability combined with capacity for rapid and irregular production. Where the demand for hydrogen would justify the installation of a sodium hydroxide recovery plant, a more economical method of generation would undoubtedly be used.

4. PRODUCTION OF SODIUM HYDROXIDE IN THE GENERATOR FROM SODIUM CARBONATE AND LIME.

Another possibility which suggested itself was that of using lime and sodium carbonate in the generator to obtain sodium hydroxide which in turn will react with ferrosilicon and produce hydrogen. The advantages to be expected from this method if successful were of the same character but of smaller magnitude than replacement of sodium hydroxide by lime.

Experiments in this connection were made by introducing into a solution of sodium carbonate an amount of lime sufficient not only to react completely with the sodium carbonate

in the first place, but also to precipitate calcium silicate and reconvert the sodium silicate after the reaction to sodium hydroxide. The reactions expected were as follows:



The curves of figure 3 show the results obtained with solutions containing the equivalent of 20 per cent of sodium hydroxide. The effect of reducing the ratio of alkali to ferrosilicon is very marked and is much greater than when pure sodium hydroxide is used. Under one condition, represented by curve *D*, the hydrogen yield during 30 minutes was only about one-third that obtained from an equivalent solution of sodium hydroxide under the same conditions, and the maximum yield obtainable even when a large excess of alkali was used (curve *A*) was only 89 per cent of the yield from sodium hydroxide solutions in large excess.

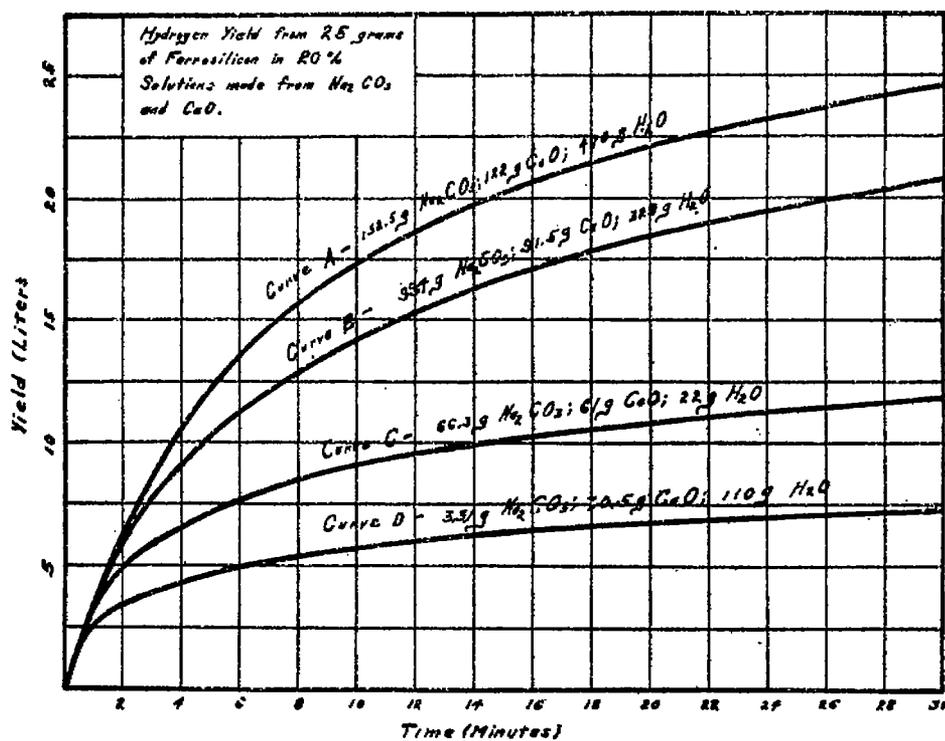


FIG. 3.

Figure 4 shows the results obtained by the use of solutions equivalent to 12.5 per cent sodium hydroxide solutions. It is noteworthy that as much hydrogen was obtained from a 12.5 per cent as from a 20 per cent solution when the ferrosilicon and alkali were used in the same ratio, and that the addition of a large excess of lime is a positive detriment. Both these facts are probably due to the viscosity of the solutions, the inclusion of sodium hydroxide in the precipitates, or the coating of the ferrosilicon with precipitates which prevent the access of the solution.

The experiments represented in figure 5 were made to determine the most favorable concentration of solution using a given ratio of alkali to ferrosilicon. It is clear that a 12.5 per cent solution (curve *A*) gives a better result than a 10 per cent solution (curve *B*) and a very much better result than a 20 per cent solution (curve *O*).

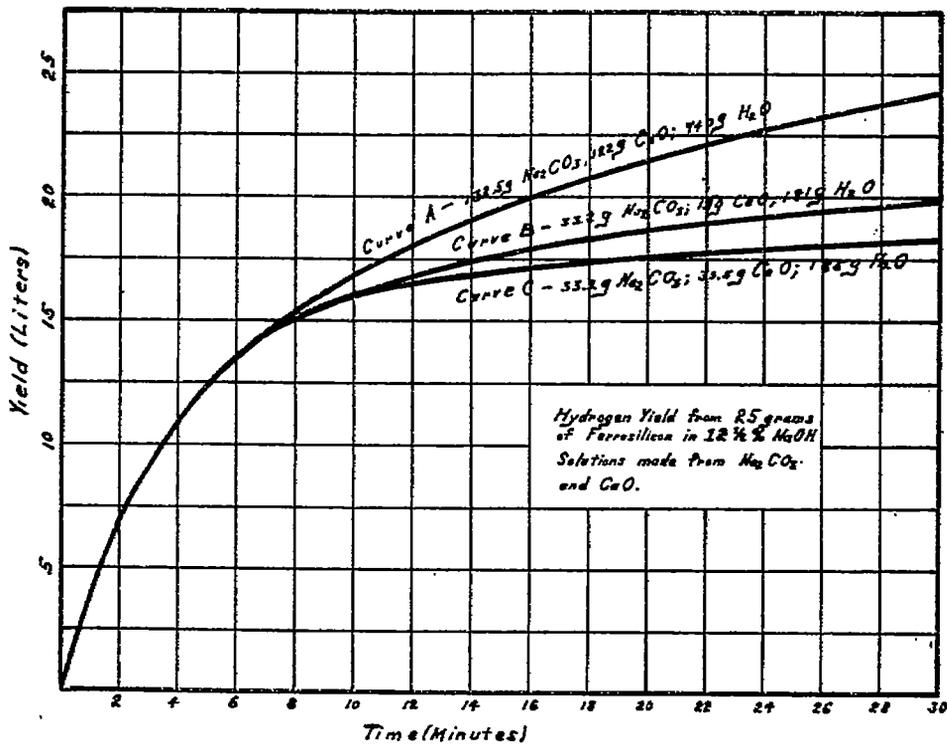


FIG. 4.

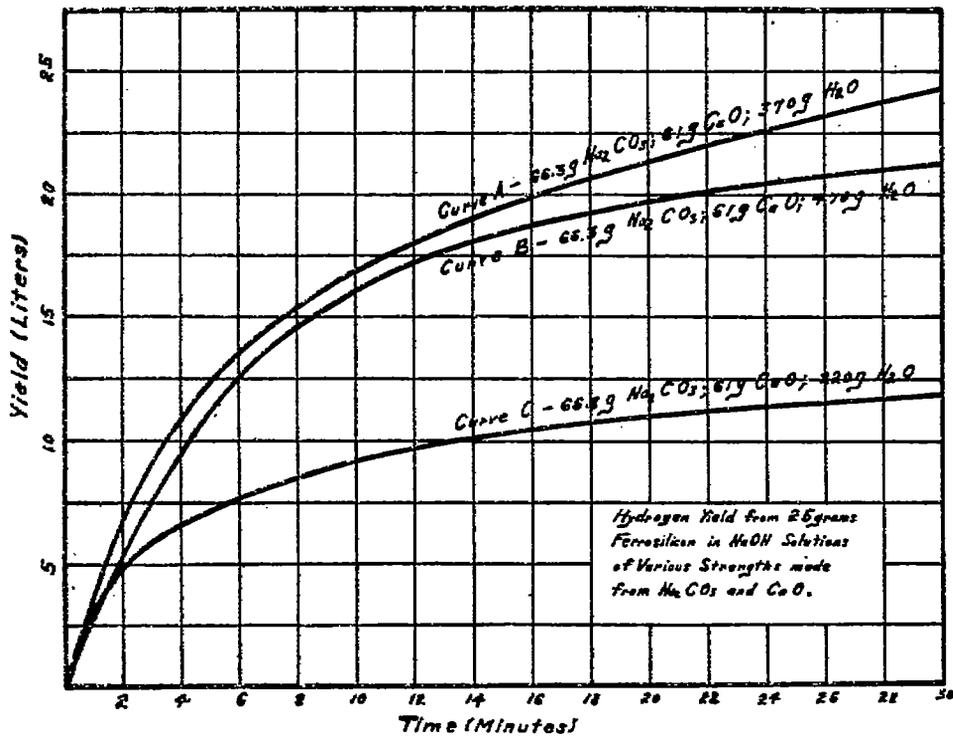


FIG. 5.

5. SUMMARY AND CONCLUSIONS.

The following conclusions may be reached from the above experiments:

1. That lime can not be used alone to replace sodium hydroxide in the generation of hydrogen from ferrosilicon and water.
2. That it is impracticable to recover sodium hydroxide from the generator sludge by the use of lime because the necessary equipment would destroy the advantages of portability and capacity for large and irregular production.
3. That it is possible but impracticable to substitute sodium carbonate and lime for sodium hydroxide in the generation of hydrogen.